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**Research Article**

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# Synthesis and characterization of NiSe and Doped NiSe: Mn

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## ABSTRACT

*Nickel selenide nano particles has been successfully synthesized from the reaction of nickel acetate [$(CH_3COO)_2$ $Ni.4H_2O$] with sodium selenite ($Na_2SeO_3$) in the presence of glycerol as capping agent and hydrazine hydrate ($N_2H_4$. $H_2O$) as reductant at 90°C for 6.30 hours through simple hydrothermal method. Doped NiSe:Mn is synthesized by chemical co-precipitation method using $NiCl_2.6H_2O$, $Na_2SeO_3$, $MnCl_2.4H_2O$ and polyvinyl pyrrolidone (PVP) which act as reductant and capping agent at room temperature. NiSe and doped NiSe:Mn were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-visible , infrared spectroscopy (IR) and photoluminescence (PL) spectra.*

**Key words**: Nano particles, NiSe, NiSe:Mn, hydrothermal, co-precipitation.

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## INTRODUCTION

The study of metal chalcogenides, their synthesis and characterization has attracted recently in the field of nanotechnology. Many metal chalcogenides find application in the field of medicine like iron oxide, in industries like zinc oxide and as semiconductors. Various techniques have been employed for the synthesis of metal chalcogenides like chemical method, hydrothermal process, solvothermal, CVD, ultrasonic synthesis [1-6], using poly vinyl alcohol (PVA) and cetyl trimethyl ammonium bromide (CTAB) as surfactants. The doped metal chalcogenides have attracted more attention and literature survey reveals that many such chalcogenides have successfully been synthesized [7-10]. In this paper an attempt has been taken to synthesis NiSe by hydrothermal route and doped NiSe:Mn through co-precipitation method. Effect of doping on the morphology has been studied by using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FT-IR), UV-Visible spectroscopy and the effect on photoluminescence property was compared using photoluminescence (PL) technique.

## EXPERIMENTAL SECTION

All the chemicals used during the experiments were analytical grade and were used as such without further purification. For NiSe synthesis, the chemicals used were (6.967g), sodium selenite (4.844g), hydrazine hydrate and glycerol as capping agent. For NiSe:Mn synthesis, $NiCl_2.6H_2O$ (1.1885g), $Na_2SeO_3$ (0.8645g), $MnCl_2.4H_2O$ (0.0324g) using PVP as capping agent.

FTIR absorption spectra were recorded over 4000 – 40 $cm^{-1}$ wave number region at a resolution of 8 $cm^{-1}$ with 1024 scans using deuterated tri glycine sulfate (DTGS) detector. The powders were investigated by FE-SEM. The machine was operated at 12 KV at a working distance of 15mm to identify the morphological properties of powders. PL spectra of the samples were taken using alcohol as solvent. The spectra were recorded between 370–770nm. UV spectra of the samples were taken using alcohol as solvent. The spectra were recorded between 200–800 nm. EDX analysis was carried out using FE-SEM spectrometer prior to SEM analysis. The machine was operated with a voltage of 16Kev. XRD analysis was carried out in the scan range of 10.000 – 70.000, with a scan speed 10.000

(deg/min). X-ray tube was operated at a voltage of 40.0 (kV).

### *Synthesis of NiSe*

Nickel acetate (70 ml of 0.4 M) and sodium selenite (70 ml of 0.4 M) with a stoichiometric ratio of 1:1 were dissolved in deionised water. To this solution 60 ml of glycerol and hydrazine hydrate (20 ml of 80 %) was added with constant stirring. The solution is kept for heating at 90 °C in a mantle for 6 h. In addition, of hydrazine hydrate, the yellowish green color slowly changed to blue which turned to black on heating. The black precipitate was washed with deionised water and absolute alcohol several times to remove glycerol and other impurities. Finally, it was dried at 100 °C for one hour. The suggested mechanism is:

(i) $NiCl_2.6H_2O \longrightarrow Ni^{2+} + 2Cl^{-} + 6H_2O$

(ii) $Na_2SeO_3 \longrightarrow 2Na^{+} + SeO_3^{2-}$

(iii) $Ni^{2+} + SeO_3^{2-} \longrightarrow Na_2SeO_3$

(iv) $SeO_3^{2-} \xrightarrow{\text{hydrazine hydrate}} 2Se^{2-} + 3O_2$

(v) $Ni^{2+} + Se^{2-} \longrightarrow NiSe$

### *Synthesis of NiSe:Mn*

$NiCl_2.6H_2O$ (25 ml of 0.2 M) and $Na_2SeO_3$ (25 ml of 0.2 M), with a stoichiometric ratio of 1:1 were dissolved in 25 ml of deionised water drop by drop gradually. To this solution, 10 ml of $MnCl_2$ (10 ml of 0.02 M) and PVP (5 ml of 0.0002 M) is added drop by drop with constant stirring. This solution was kept in a magnetic stirrer at room temperature for 5 h. The yellowish green precipitate obtained was washed with distilled water and acetone several times. Finally, it was kept for drying at 100 °C for one and half hours. In this method PVP acts as surfactant as well as reducing agent at room temperature [12]. The suggested mechanism is:

(i) $NiCl_2.6H_2O \longrightarrow Ni^{2+} + 2Cl^{-} + 6H_2O$

(ii) $Na_2SeO_3 \longrightarrow 2Na^{+} + SeO_3^{2-}$

(iii) $Ni^{2+} + SeO_3^{2-} \longrightarrow Na_2SeO_3$

(iv) $SeO_3^{2-} \xrightarrow{PVP} Se^{2-} + 3O_2$

(v) $Ni^{2+} + Se^{2-} \longrightarrow NiSe$

(vi) $NiSe + Mn \xrightarrow{PVP} NiSe: Mn$

## RESULTS AND DISCUSSION

Figures 1 and 2 show XRD patterns of NiSe and doped NiSe:Mn . XRD is a powerful non-destructive technique for characterizing crystalline materials. It provides information about the structures, phases, preferred crystal orientations and other structural parameters such as average grain size, crystallinity, strain and crystal defects. XRD peaks are produced by constructive interference of a monochromatic beam of X-rays scattered at specific angles from each set of lattice planes in a sample. The peak intensities are determined by the distribution of atoms within the lattice. The XRD plot of NiSe shows sharp peaks indicating crystallinity. The highest peak positions corresponds to the other rhombic structure with cell edges corresponding to a=1.574 nm b=2. 341nm and c=0.6926 nm with axial angles 90° between the planes. The width of the XRD plots of NiSe:Mn shows a decrease indicating the increase in size of particles. This can be attributed due to doping of Mn, the particles occupy in between NiSe particles resulting in an increase in size. The peak of the plot corresponds to orthorhombic structure with edge length a=0.756nm, b=0.826nm and c=1.194nm (calculated using JCPDS - PCPDFWIN VERSION 2.3 JUNE 2002 JCPDS – ICDD).

Figures 3 and 4 show Fe-SEM pictures of the samples NiSe and doped NiSe:Mn. SEM provides information on the surface morphology. It is seen clearly that the size and shape of the molecules of NiSe changes due to doping. A great difficulty was observed while taking Fe-SEM images of Mn doped NiSe. The sample from the tray was moving away when electron beam was passed. This can be attributed due to the presence of a large number of unpaired electrons in Mn, which interact with the electron beam used during the analysis. It was also observed that the appearance of *broccoli* shaped NiSe changes to a *broken cluster shape*. This is partly attributed due to doping and also due to the presence of hydrazine hydrate in the synthesis of NiSe [11] and absence of the same in the synthesis of doped NiSe:Mn. It is also seen that XRD and SEM results are in great agreement.

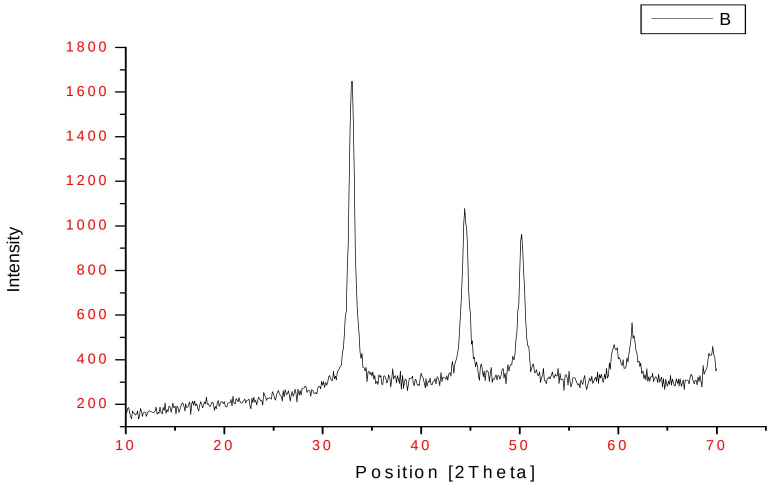


**Fig – 1 XRD patterns of NiSe**

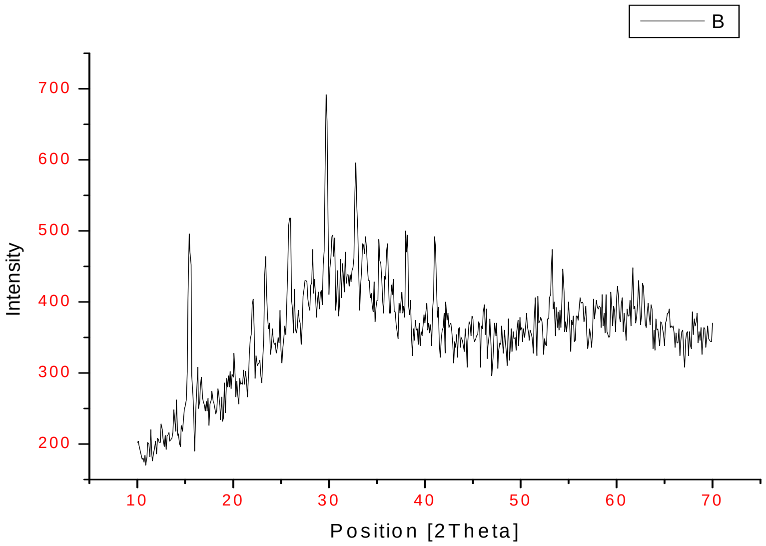
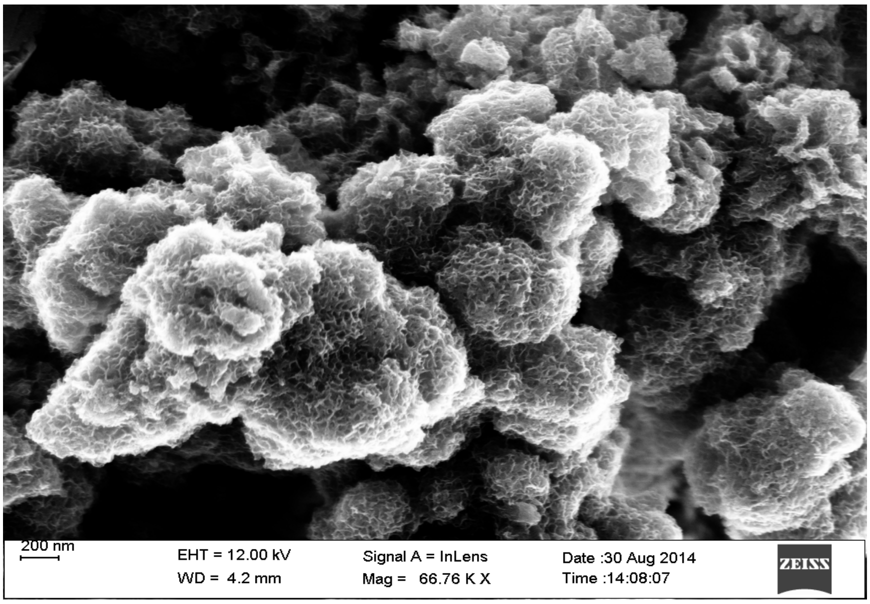


**Fig – 2 XRD patterns of doped NiSe:Mn**



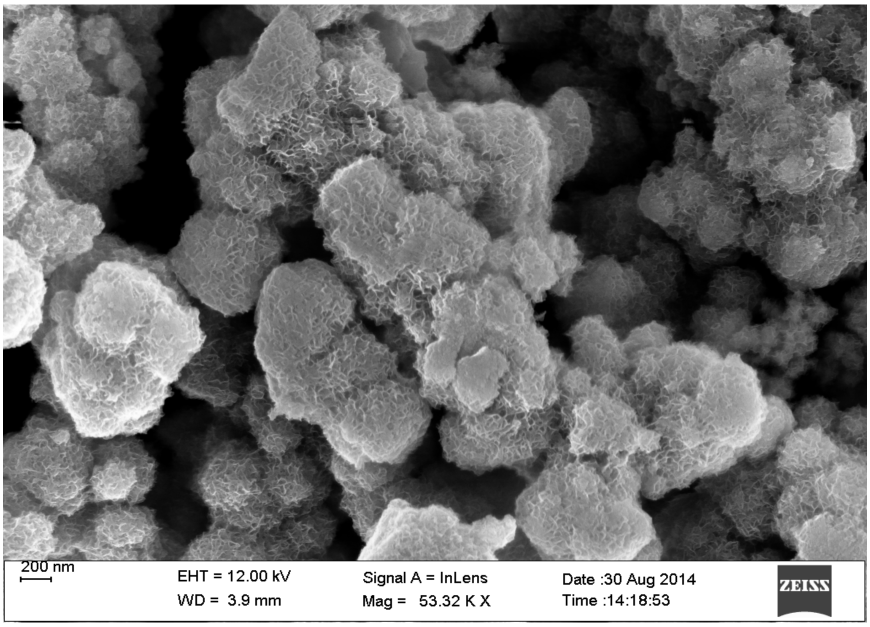
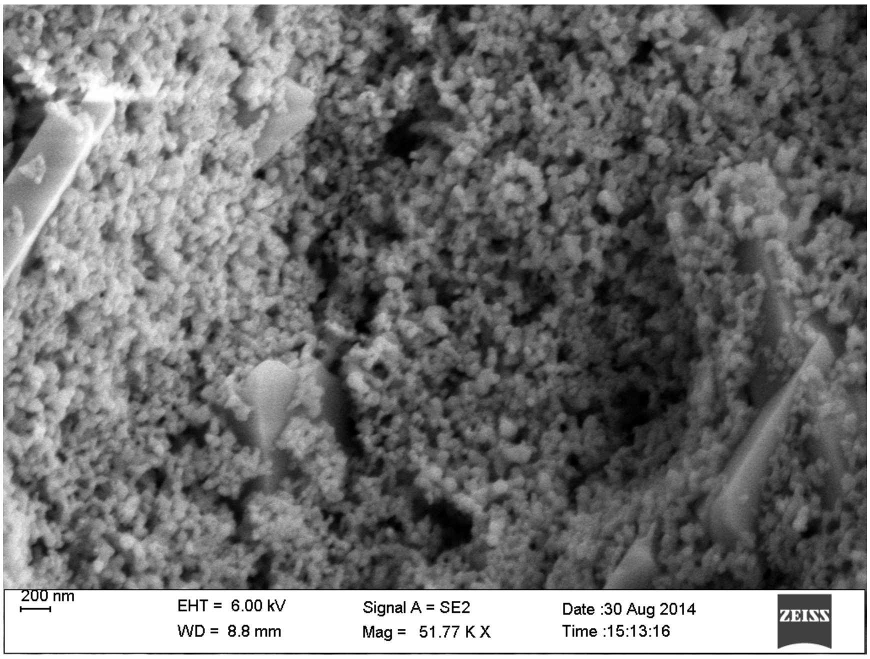


**Fig – 3 SEM images of NiSe**

Figures 5 and 6 show EDX result of NiSe and NiSe:Mn which confirms the presence of the respective elements. One of the impressive features of semiconductors is their ability to emit light. Upon excitations with wavelength shorter or equivalent to the absorption onset, an electron is promoted from the valence band to the conduction band and upon relaxation a photon of light is emitted. The minimum photon energy that is required to excite an electron into the conduction band is associated with the band gap of a material. PL describes the phenomenon of light emission from any form of matter after the absorption of photons. It is one of many forms of luminescence and is initiated by photo excitation. The most common use of PL is band gap or band to band transitions determination and detection of impurity and defect.



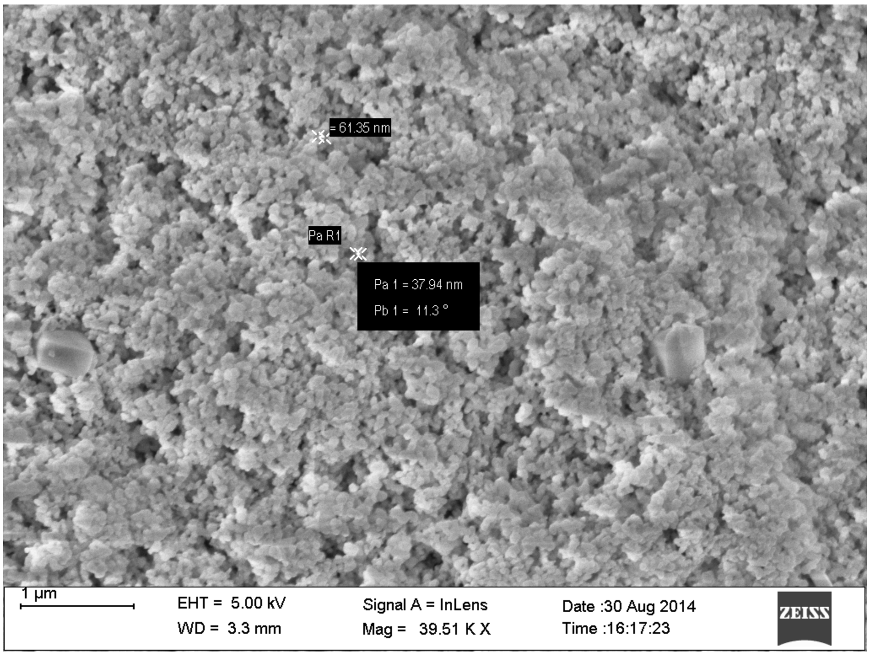


**Fig – 4 SEM images of doped NiSe:Mn**

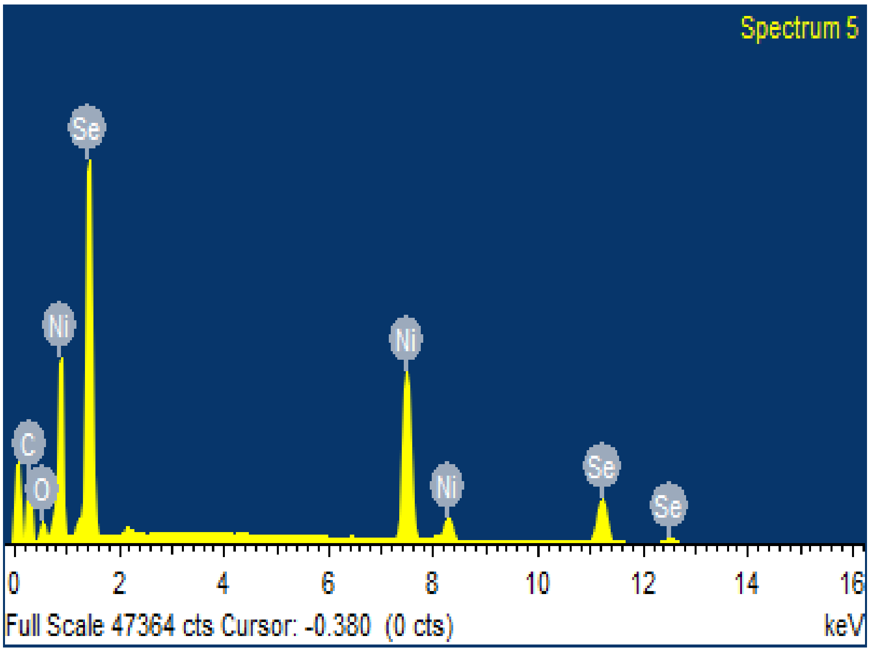


**Fig – 5 EDX result of NiSe**

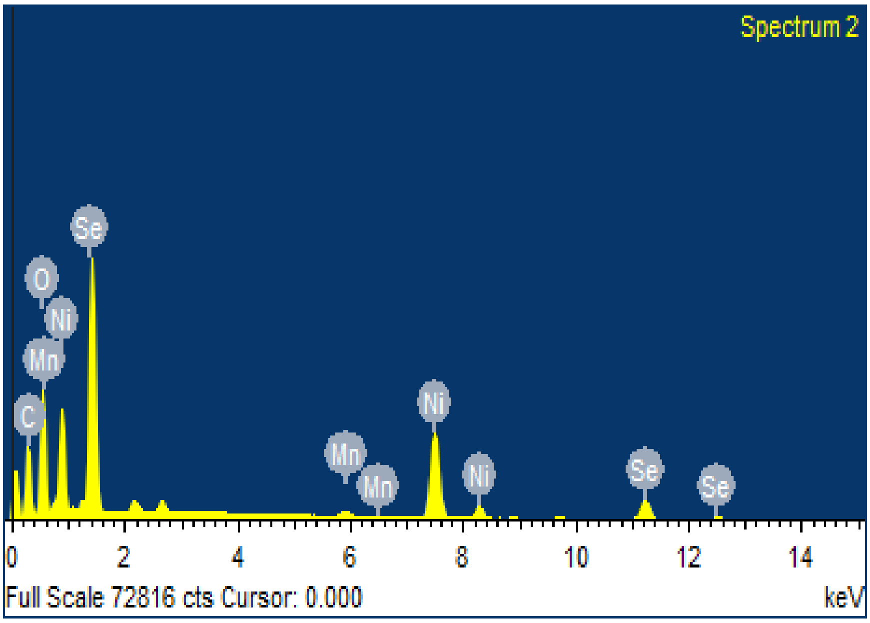


**Fig – 6 EDX result of doped NiSe:Mn**

Figures 7 and 8 show PL spectra of NiSe and doped NiSe:Mn. The PL spectra of NiSe shows a band gap of 440nm = 2.8178eV. On doping with Manganese, the band gap increases from 440nm to 700 nm, thereby decreasing the band gap energy to 1.7712eV. This shows that the conductivity of NiSe has increased on doping with Manganese. The intensity of the peak also shows a red shift from blue end.

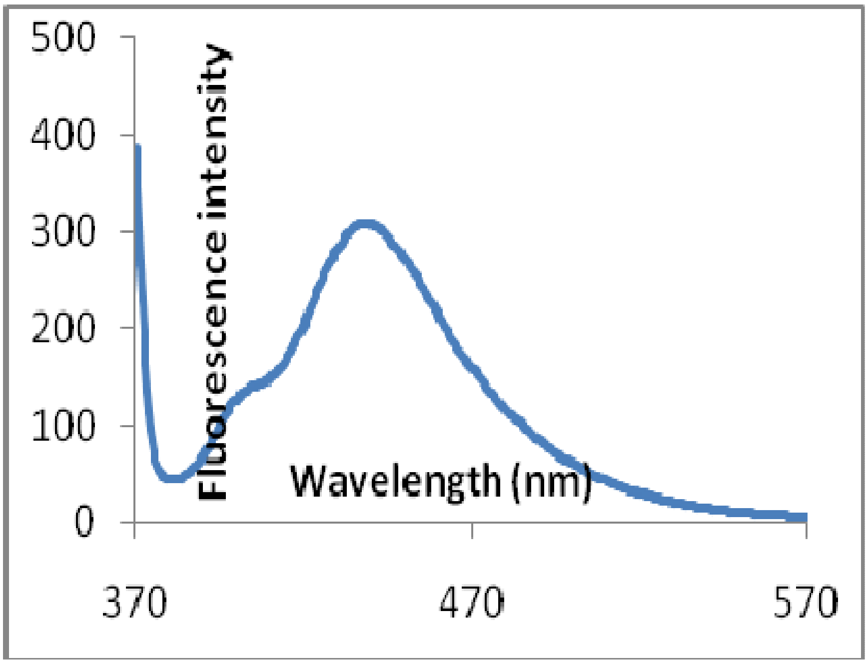


**Fig – 7 Solution PL spectra of NiSe**

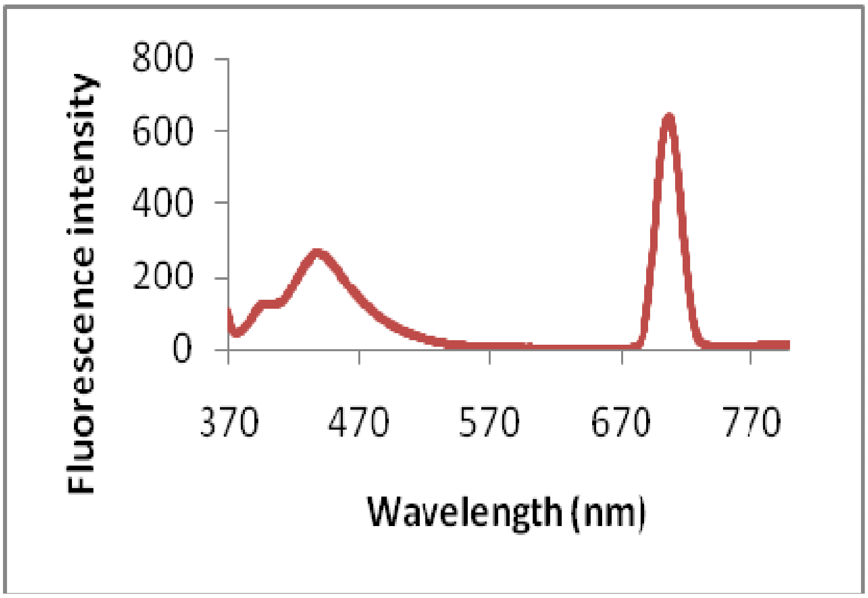


Fig – 8 Solution PL spectra of NiSe:Mn

Figures 9 and 10 show absorption spectra of NiSe and doped NiSe: Mn obtained in the wavelength range of 190-800nm. The absorption peak of NiSe is obtained at about 354nm. It is observed from the absorption spectra of NiSe:Mn that there is no observable difference in the spectra after doping.

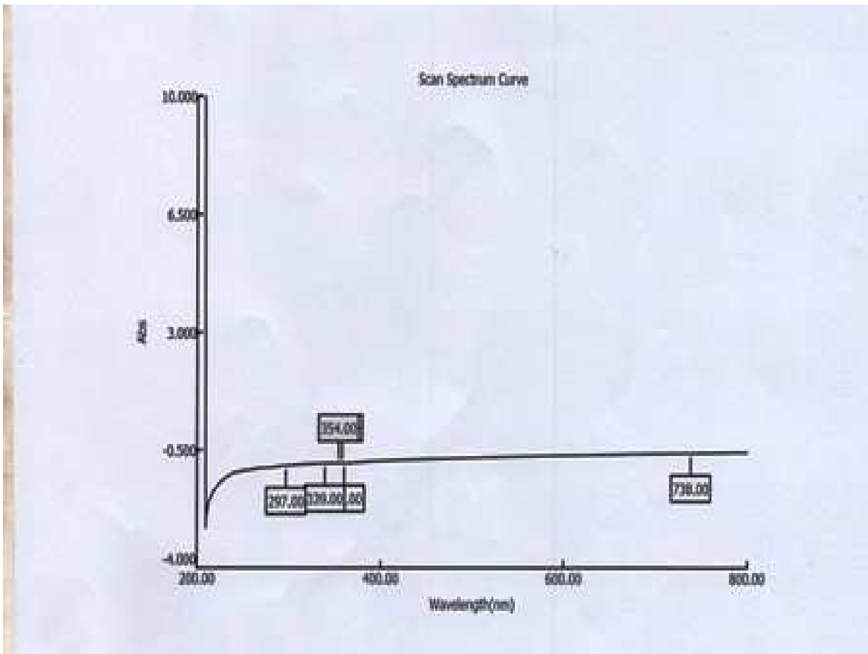


Fig – 9 UV result of NiSe

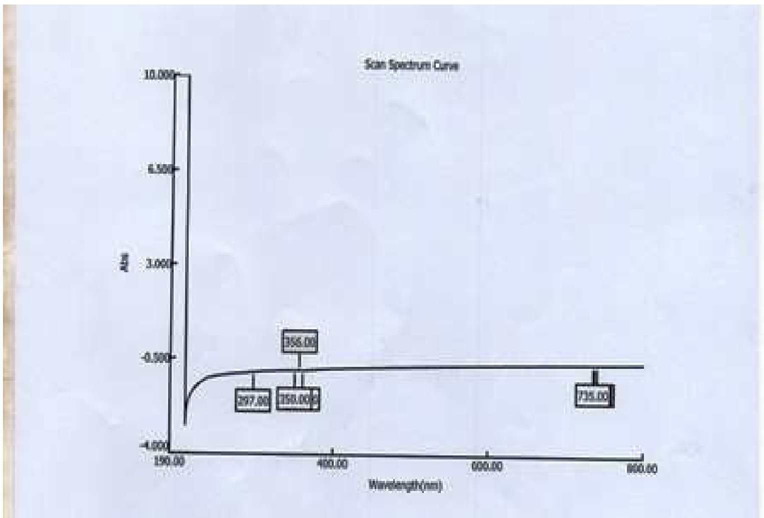


Fig – 10 UV result of NiSe:Mn

FT-IR spectra of NiSe and NiSe:Mn are given in Fig 11 and 12. In figure 11, the most intense and broadest band appears at 3458 $cm^{-1}$. This can be associated with the vibrational modes of –OH hydroxyl groups bonded with external hydrogen and / or atoms of the chalcogenides structural network. A similar absorption frequency appears at 3450 $cm^{-1}$ in figure 12. The other, much weaker band, associated with the adsorbed molecule $H_2O$ which appear at 1658 $cm^{-1}$. The reason for the appearance of these absorption bands is mostly due to the moisture absorbed by the sample from the environment during the sample preparation and due to IR measurement. The oxides are among the impurities that are strongly dependent on the chemical composition of chalcogenides. In all IR spectra, absorption bands are present related to vibrations of oxygen atoms bonded to basic elements or to carbon impurity atoms. A band appearing at 800-70 $cm^{-1}$ can be due to the presence of Ni-O bonds in the powders. The broad and asymmetric band centered at 578 and 499 $cm^{-1}$ can be dependent on the composition, attributed to the vibrational mode of Se-O bonds.

| | I | II |
|---|---|---|
| γO-H | 3458 | 3450 |
| γC-H | 2922 | 2931 |
| γNi-O | 802, 704 | 719 |
| γSe-O | 578, 499 | 501 |

This table shows the different vibrational frequencies corresponding to the various modes of vibrations confirming the presence of NiSe:Mn.

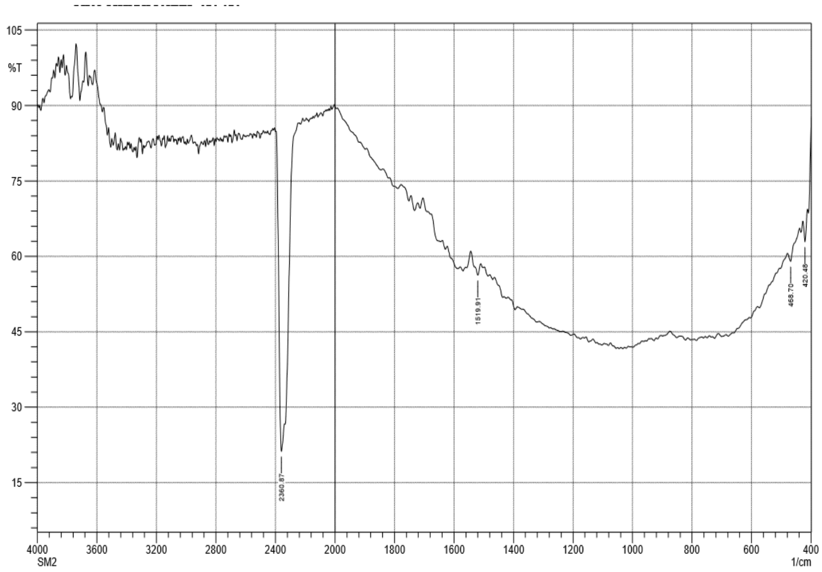


Fig – 11 IR result of NiSe

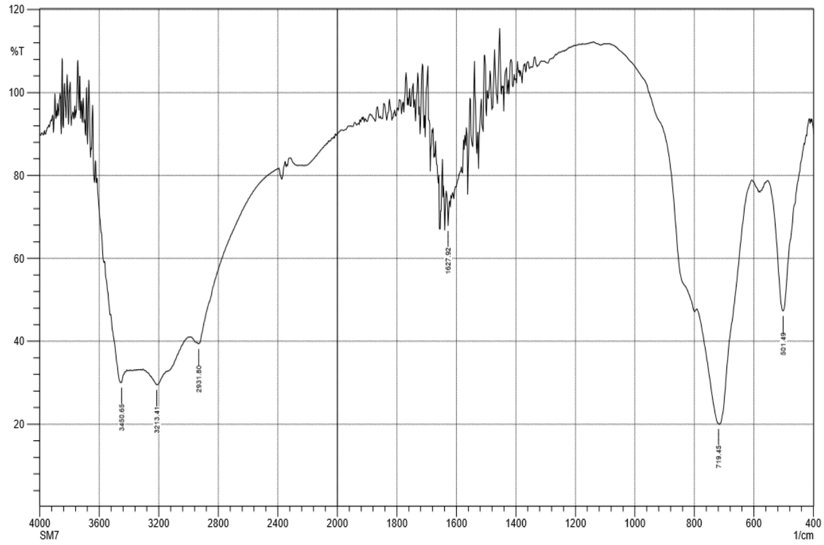


**Fig – 12 IR result of NiSe:Mn**

## CONCLUSION

NiSe and doped NiSe: Mn were successfully synthesized by hydrothermal and co-precipitation processes respectively. EDX analysis confirms the presence of these elements. SEM and XRD revealed that the particle size and shape is greatly influenced by doping. Broccoli shaped NiSe obtained changed to broken cluster shape after doping with Manganese. The possible reason for the change in the structure has also been explained. PL spectra revealed that conductivity of NiSe is enhanced by doping with Manganese. There is no observable difference noticed in absorption spectra of NiSe and doped NiSe:Mn. IR spectrum also reveals the formation of NiSe and Zn doped NiSe.

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