Synthesis and characterization NiSe and cobalt doped NiSe

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ABSTRACT

Nickel selenide nano particles has been successfully synthesized from the reaction of Nickel acetate [(CH$_3$COO)$_2$ Ni.4H$_2$O] with sodium selenite (Na$_2$SeO$_3$)in the presence of glycerol as capping agent and hydrazine hydrate (N$_2$H$_4$.H$_2$O)as reductant at 90°C for 6.30hours through a simple thermal reduction process. Doped NiSe: Cois synthesized by chemical Co-precipitation method using Nickel acetate [(CH$_3$COO)$_2$ Ni.4H$_2$O], Sodium selenite (Na$_2$SeO$_3$),Cobalt acetate[(CH$_3$COO)$_2$ Co.4H$_2$O] and PVP which act as reductant and capping agent at room temperature. NiSe and doped NiSe:Co were characterized by X-ray diffraction (XRD), Scanning electron microscopy(SEM), Visible Ultra violet spectroscopy (UV), infra red spectroscopy (IR), Energy dispersive X-ray spectroscopy (EDX)and photoluminescence (PL) spectra.

Key words: Nano particles, NiSe, NiSe:Co, Thermal reduction, Co-precipitation
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INTRODUCTION

In the field of nano sciences, now-a-days synthesizing the nano materials and their characterization has taken a very important role. The due attention given to the preparation and characterization of metal chalcogenides has increased to a greater extent due to their properties and potential applications in different diverging fields like photovoltaics, hydrogen production, lithium battery, energy storage, photo catalysis, sensors and many more. Various techniques have been employed for the synthesis of metal chalcogenides like chemical method, hydrothermal process, solvothermal, CVD, ultrasonic synthesis, sol-gel combustion method[1-8], using poly vinyl alcohol(PVA), cetyl trimethyl ammonium bromide (CTAB) as surfactants. The doped metal chalcogenides have attracted more attention and many such chalcogenides are successfully synthesized [9-13].More attention is also given to doped metal chalcogenides which are synthesized and compared [14-16].In this paper an attempt was taken to synthesis NiSe by hydrothermal route then doped NiSe:Co was synthesized 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 Infra red spectroscopy (FT-IR),Visible Ultra violet spectroscopy (UV) and the effect on photoluminescence property was compared using Photoluminescence (PL) technique.
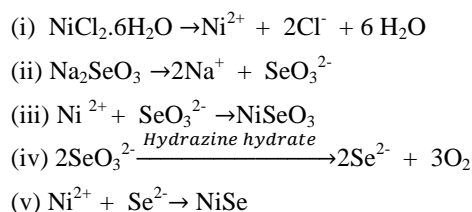
EXPERIMENTAL SECTION

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 nickel acetate (6.967g), sodium selenite (4.844g), hydrazine hydrate and glycerol as capping agent. For NiSe:Co synthesis, Nickel acetate (1.244g), Sodium selenite(0.865g), Cobalt acetate (0.0498g) using PVP as capping agent. The powders were investigated by FE-SEM.

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The machine was operated at 12 KV at a working distance of 15mm to identify the morphological properties of powders. EDX analysis was carried out using FE-SEM spectrometer prior to SEM analysis. The machine was operated with a voltage of 16Kev. PL spectra of the samples were taken using alcohol as solvent. The spectra were recorded between 370 – 770nm.All FTIR absorption spectra were recorded over 4000 – 40 cm^{-1} wave number region at a resolution of 8cm^{-1} with 1024 scans using deuterated tri glycine sulfate (DTGS) detector. 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 (k.V). Visible UV spectra of the samples were taken using alcohol as solvent. The spectra were recorded between 200 – 800 nm.
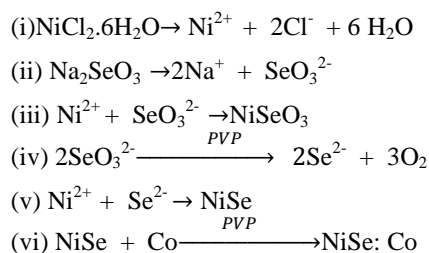
Synthesis of NiSe – Using glycerol
Nickel acetate (70ml of 0.4M) and sodium selenite (70ml of 0.4M) with a stoichiometric ratio of 1:1 were dissolved in deionized water. To this solution 60ml of glycerol and 20ml of hydrazine hydrate (80%) were added with constant stirring. The solution is kept for heating at 90°C in mantle for6hours. On addition of hydrazine hydrate, the yellowish green colour slowly changed to blue which turned to black on heating. The black precipitate was washed with deionized 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 as follows:

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

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

(iii) $Ni^{2+} + SeO_3^{2-} \rightarrow NiSeO_3$

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

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

Synthesis of NiSe:Co – Chemical Co-precipitation process using PVP
Nickel acetate (25ml of 0.2M) and sodium selenite (25ml of 0.2M)with a stoichiometric ratio of 1:1 were dissolved in 25ml of deionized water drop by drop gradually. To this solution 10ml of cobalt acetate (0.02M) and 5 ml of PVP (0.0002) is added drop by drop with constant stirring. This solution was kept in magnetic stirrer at room temperature for 4 hours. The yellowish green precipitate obtained was washed with distilled water and acetone several times. In this method PVP acts as reducing agent as well as surfactant [17]. Finally it is kept for drying at 100°C for one hour. The suggested mechanism is as follows:

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

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

(iii) $Ni^{2+} + SeO_3^{2-} \rightarrow NiSeO_3$

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

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

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

RESULTS AND DISCUSSION

Figure 1a and 1b show XRD patterns of NiSe and doped NiSe:Co. 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 mono chromatic beam of X-rays scattered at specific angles from each set of lattice planes in a sample.
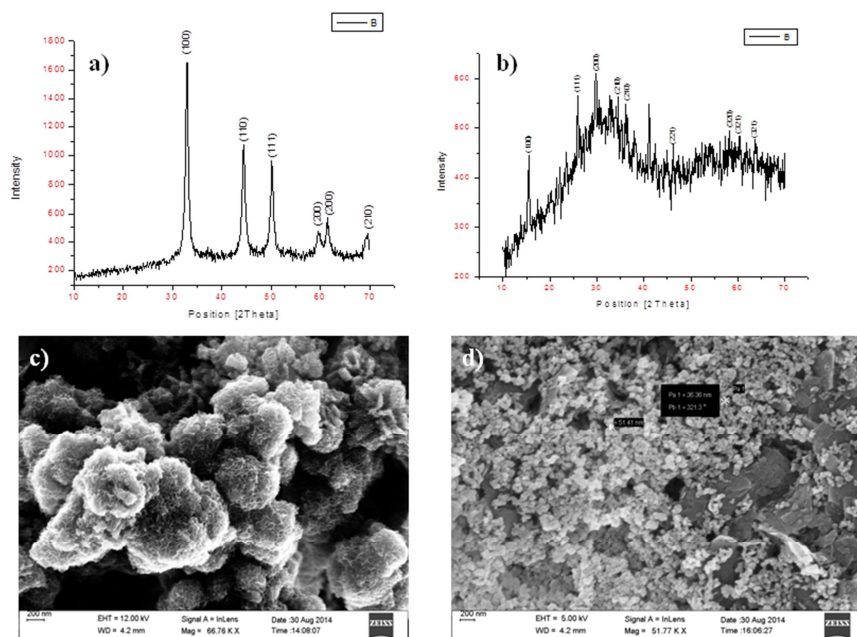
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Figure 1a) XRD patterns of NiSe b) XRD patterns of doped NiSe:Co c) SEM images of NiSe and d) SEM images of doped NiSe:Co

The miller indices values (hkl) for the various peaks in NiSe are (Table 1) calculated as shown below:

Table 1 Calculation of hkl values of NiSe

2 Theta	D	$V = 1000 / d^2$	V / C.F	hkl
32.92	2.718	135.37	1.28	100
44.42	2.037	241.02	2.28	110
50.15	1.817	302.93	2.867	111
59.73	1.547	417.88	3.955	200
61.43	1.508	439.75	4.162	200
69.37	1.353	546.45	5.172	210

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 cell edges a=1.574 nm, b=2.341nm and c=0.6926nm with axial angles 90° between the planes [18]. The XRD plot of NiSe:Co shows sharp peaks indicating crystallinity. The width of the XRD plots of NiSe:Coshows a decrease indicating the increase in size of particles, which is also seen from Fe-SEM plots. This can be attributed due to doping of Co, the particles occupy in between NiSe particles resulting in increase in size. The peak of the plot corresponds to edge length a=1.220nm, b=0.3497nm and c=0.8433nm with axial angle β= 103.15°(calculated using JCPDS). The slight change in axial angles of NiSe after doping is due to introduction of Co atoms in between NiSe particles and also due to increase in size of particles.

The lattice values for the various peaks in NiSe:Co are calculated (Table 2) as follows:

Table 2 Calculation of hkl values of NiSe:Co

2 Theta	D	$V = 1000 / d^2$	V / C.F	hkl
15.44	5.733	30.42	1.00	100
25.9	3.430	84.99	2.793	111
29.7	3.005	110.74	3.640	200
34.6	2.590	149.07	4.900	210
36.2	2.478	162.86	5.353	210
47.5	1.912	273.59	8.993	221
58.18	1.584	398.56	13.10	320
60.2	1.535	424.44	13.95	321

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Figure1c and 1d shows Fe-SEM pictures of the samples NiSe and doped NiSe:Co. SEM provides information of the surface morphology. It is seen clearly that the size and shape of the molecules of NiSe changes due to doping. It can be observed that the broccoli shaped NiSe changes to strewn flowers shape. This is partly attributed due to doping and also due to the presence of hydrazine hydrate in the synthesis of NiSe [19], reaction temperature and absence of the same, room temperature in the synthesis of doped NiSe:Co. Figure 2a and 2b shows EDX result of NiSe and NiSe:Co. EDX is an important tool for finding the presence of various elements in the known or unknown samples. The results confirm the presence of the Ni, Se in Figure 2a and the presence of Ni, Se, Co in Figure 2b.
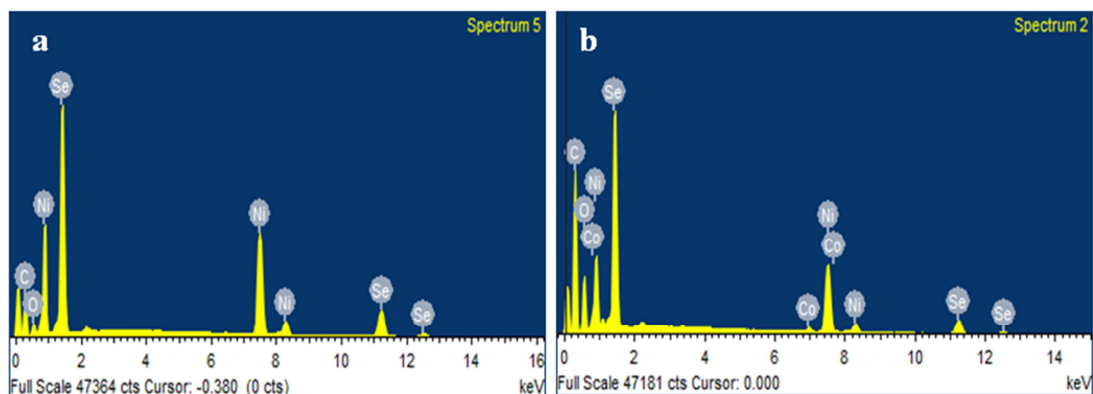

Figure 2 a) EDX result of NiSe and b) EDX result of doped NiSe:Co

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 phonon 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. Figure 3a and 3b shows PL spectra of NiSe and doped NiSe:Co. The PL spectra of NiSe shows band gap of 440nm = 2.8178eV. On doping with Cobalt, 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 Cobalt.

The intensity of the peak also shows a red shift from blue end. Figure 3c and 3d shows absorption spectra of NiSe and doped NiSe:Co obtained in wavelength range of 200-800nm. The absorption peak of NiSe is obtained at about 354nm. It is observed from the absorption spectra of NiSe:Co that there is observable difference in the spectra of NiSe after doping. The various absorption peaks obtained in case of NiSe is shown in Table 3.

Table 3 Absorption peaks of NiSe

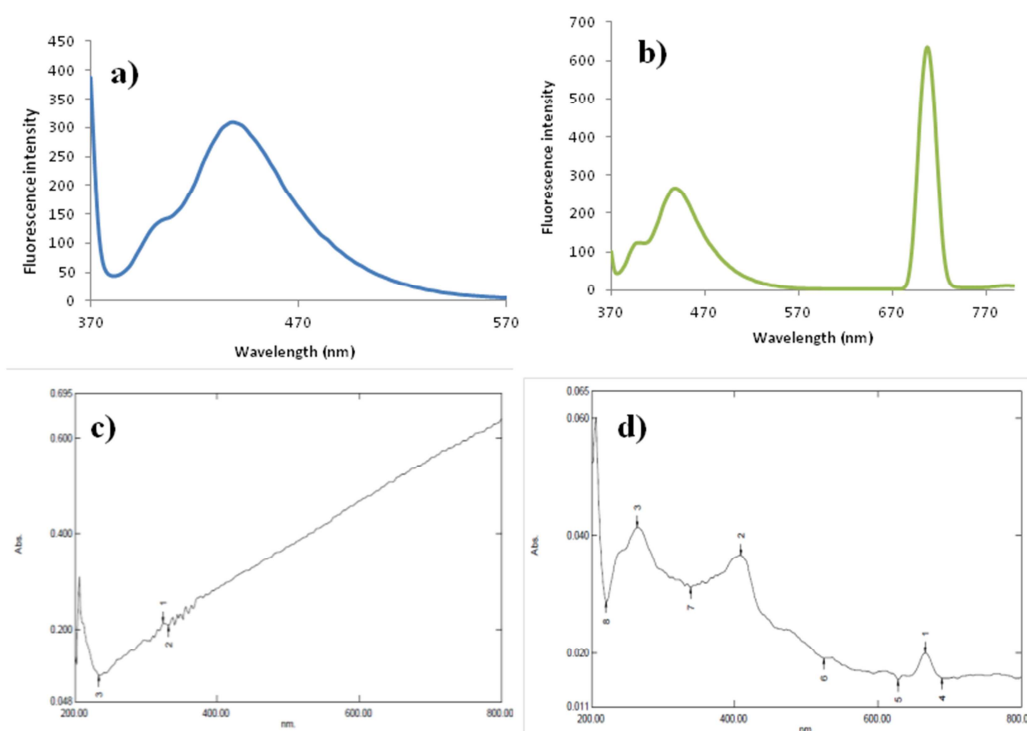| No.	P/V	Wavelength	Abs.
1	⬆	324.00	0.212
2	⬇	332.00	0.208
3	⬇	234.00	0.102

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Figure 3 a) Solution PL spectra of NiSe b) Solution PL spectra of NiSe:Co c) UV result of NiSe and d) UV result of NiSe:Co

The different absorption peaks obtained in doped NiSe:Co is shown in Table4:

Table 4 Absorption peaks obtained in doped NiSe:Co

No.	P/V	Wavelength	Abs.
1	⬆	666.00	0.020
2	⬆	408.00	0.037
3	⬆	264.00	0.041
4	⬇	690.00	0.016
5	⬇	628.00	0.015
6	⬇	524.00	0.019
7	⬇	338.00	0.031
8	⬇	220.00	0.029

The band gap energy is calculated using the expression:

$$E = \frac{h\,c}{\lambda}$$

In case of NiSe, it is found to be 0.0613×10^{-17} J which is 3.825 eV. Where as in the case of doped NiSe:Co, it is found to be 0.0298×10^{-17} J which is 1.8598 eV. It is clear from the band gap energy that there is considerable increase in conductivity of NiSe after doping with Cobalt. It is also observed that there is a red shift from blue end after doping with cobalt. This result obtained is also in good agreement with those of Photo luminescence spectroscopic analysis, though there is a mild difference in the band gap energy values. This can be attributed due to the difference in the instrumentation, operational methods and also due to the atmospheric conditions during measurements.

FT-IR spectra of NiSe and NiSe:Co are given in Figure 4a and 4b. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification

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(qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present.
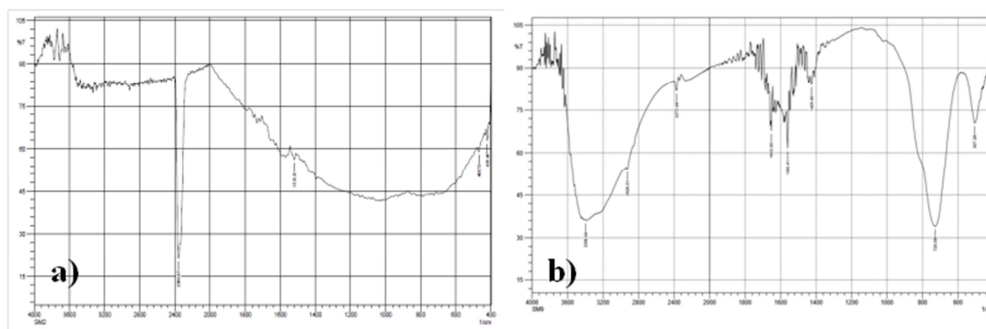

Figure 4 a) IR result of NiSe and b) IR result of NiSe:Co

The various absorption peaks and the corresponding vibration modes (Table 5) are as follows:

Table 5 Absorption peaks and the corresponding vibrational modes

NiSe		NiSe:Co	
γBond	Frequency (cm^{-1})	Bond	Frequency (cm^{-1})
γ Se-H	2360.87	γO-H	3397 , 2926
γC=O	1519.91	γSe-H	2372.44
γNi-O	468.70	γNi-O	729
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In Figure 4b, the most intense and broadest band appears at 3396 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. The absorption peaks appearing at 2931.8 cm^{-1} in Figure 4a and 2372 cm^{-1} in Figure 4b corresponds to the vibrational mode of Se-H bond. The other, much weaker band associated with the adsorbed molecule of H_2O which appearing between 1560 and 1660 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 729cm^{-1} can be due to the presence of Ni-O bonds in the powders. The band centered at 507cm^{-1} is due to vibrational mode of Co-O bonds. The intensity of the absorption band is also in agreement with the amount of various elements present in the sample shown by EDX analysis.

CONCLUSION

NiSe and doped NiSe:Co were successfully synthesized by Thermal reduction and co-precipitation process respectively. EDX analysis confirms the presence of the concerned elements. SEM and XRD revealed that the particle size and shape is greatly influenced by doping. Broccoli shaped NiSe obtained, changed to strewn flowers shape after doping with Cobalt. The possible reason for the change in the structure was also explained. PL spectra revealed that conductivity of NiSe is enhanced by doping with Cobalt. There is observable difference noticed in absorption spectra of NiSe and doped NiSe:Co which is in greent agreement with the results obtained from PL analysis. IR spectrum also reveals the formation of NiSe and Cobalt doped NiSe:Co.

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