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Synthesis and Characterization of Chromium Doped NiSe

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Abstract

Nickel selenide and chromium doped Nickel selenide have been successfully synthesized. Nickel selenide nano particles has beensynthesized 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 thermal reduction process. Doped NiSe:Cr is synthesized by chemical Co-precipitation method using Nickel Chloride* ($NiCl_2.6H_2O$)*, Sodium Selenite* (Na_2SeO_3)*, Chromium Chloride* ($CrCl_3.6H_2O$) *and PVP which act as reductant and capping agent at room temperature. NiSe and doped NiSe:Cr were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), infrared spectroscopy (IR), Visible Ultra violet spectroscopy (UV), Energy dispersive X-ray spectroscopy (EDX) and photoluminescence (PL) spectra.*

Keywords: *Co-precipitation; Nano particles; NiSe; NiSe:Cr; Thermal reduction.*

1. INTRODUCTION

In recent years, the application of nano particles has increased tremendously. For instance the following nano particles find uses in various fields: Alumino silicate in reducing trauma, iron oxide to improve MRI images, gold in manganese oxide to break down volatile organic compounds in air, quantum dots in identifying cancer cells in body and so on. The preparation and characterization of metal chalcogenides have also attracted more importance 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 (Hankare *et al.* 2010), hydrothermal process (Azam Sobhani *et al.* 2010), solvothermal, CVD, ultrasonic synthesis using poly vinyl alcohol (PVA), cetyl trimethyl ammonium bromide (CTAB) (Azam Sobhani *et al.* 2011, 2012; Azam Sobhani and Masoud Salavati-Niasari, 2014), oleic acid (Weimin Du *et al.* 2007) as surfactants. The doped metal chalcogenides have attracted more attention and many such chalcogenides are successfully synthesized (Rahdar *et al.* 2012; Kole *et al.* 2012; Soundararajan *et al.* 2009; Sunil Kumar *et al.* 2012). In this paper an attempt was taken to synthesis NiSe by hydrothermal route then doped NiSe:Cr 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), Visible Ultra violet spectroscopy (UV), Infra red spectroscopy (FT-IR) and the effect on photoluminescence property was compared using Photoluminescence (PL) technique.

2. EXPERIMENTAL METHOD

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 (6.967 g), sodium selenite (4.844 g), hydrazine hydrate and glycerol as capping agent. For NiSe:Cr synthesis, $NiCl_2.6H_2O$ (1.1885 g), Na_2SeO_3 (0.8645 g), $CrCl_2.6H_2O$ (0.0533 g) using PVP as capping agent.

The powders were investigated by FE-SEM. The machine was operated at 12 KV at a working distance of 15 mm to identify the morphological properties of powders. PL spectra of the samples were taken using alcohol as solvent. The spectra were recorded between 370-770 nm. UV spectra of the samples were taken using alcohol as solvent. The spectra were recorded between 200-800 nm. EDX

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analysis was carried out using FE-SEM spectrometer prior to SEM analysis. The machine was operated with a voltage of 16 Kev. 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). All 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 triglycine sulfate (DTGS) detector.

2.1 Synthesis of NiSe-using glycerol

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 deionized water. To this solution 60 mL of glycerol and certain amount of hydrazine hydrate (20 mL of 80%) were added with constant stirring. The solution is kept for heating at 90 °C in mantle for 6 hrs. 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:

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

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

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

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

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

2.2 Synthesis of NiSe : Cr-Chemical Co-precipitation process using PVP

$NiCl_2.6H_2O$ (25 mL 0.2 M) and Na_2SeO_3 (25 mL 0.2 M), with a stoichiometric ratio of 1:1 were dissolved deionized water drop by drop gradually. To this solution 10 mL of $CrCl_3$ (0.02 M) and a certain amount of PVP (0.002 M) is added drop by drop with constant stirring. This solution was kept in magnetic stirrer at room temperature for 4.30 hrs. The yellowish green precipitate obtained was washed with distilled water and acetone several times. Finally it is kept for drying at 100 °C for one hour. In this method PVP acts as surfactant as well as reducing agent at room temperature (Cristina E. Hoppe *et al*. 2006). The suggested mechanism is:

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

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

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

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

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

(vi) $NiSe + Cr \rightarrow NiSe:Cr$

3. RESULTS & DISCUSSION

Fig. 1 and 2 shows XRD patterns of NiSe and doped NiSe:Cr. 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. The peak intensities are determined by the distribution of atoms within the lattice. The XRD plot of NiSe shows sharp peaks indicating crystallinity. The bond parameters corresponding to the highest peak positions have the value a=1.574 nm, b=2.341 nm and c=0.6926 nm with axial angles 90° between the planes. The XRD plot of NiSe:Cr shows sharp peaks indicating crystallinity. The width of the XRD plots of NiSe:Cr shows a decrease indicating the increase in size of particles, which is also in agreement with Fe-SEM plots. This can be attributed due to doping of Cr, the particles occupy in between NiSe particles resulting in increase in size. The peak of the plot corresponds to the edge length a=b=0.8298 nm and c=1.156 nm with axial angles 90° between the planes (Calculated using JCPDS). The slight change in axial distance of NiSe after doping is due to introduction of Cr atoms in between NiSe particles.

Fig. 3 and 4 shows Fe-SEM pictures of the samples NiSe and doped NiSe:Cr. 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 (Sasthaa Begum *et al.* 2015). It can be observed that the broccoli shaped NiSe changes to buster cluster shape. The size of particles of NiSe ranges from 13 nm to 31.82 nm seems to increase after doping with Chromium. Doped particles size ranges from 24 nm to 49 nm. This is partly attributed due to doping and also due to the presence of hydrazine hydrate in the synthesis of NiSe (Monica Debbarma *et al.* 2013) and absence of the same in the synthesis of doped NiSe:Cr. This shows that XRD and SEM results are in great agreement.

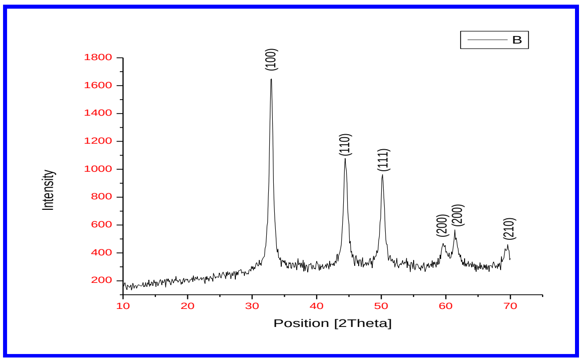

Fig. 1: XRD plot of NiSe

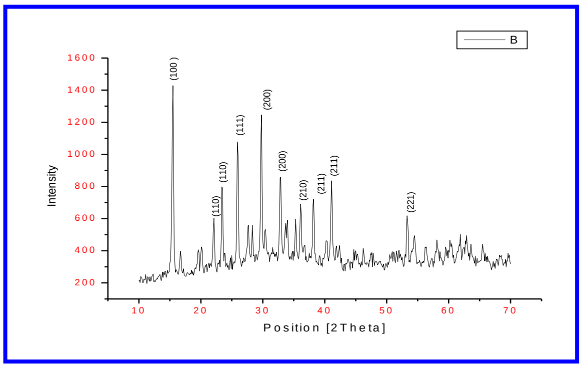

Fig. 2: XRD plot of NiSe:Cr

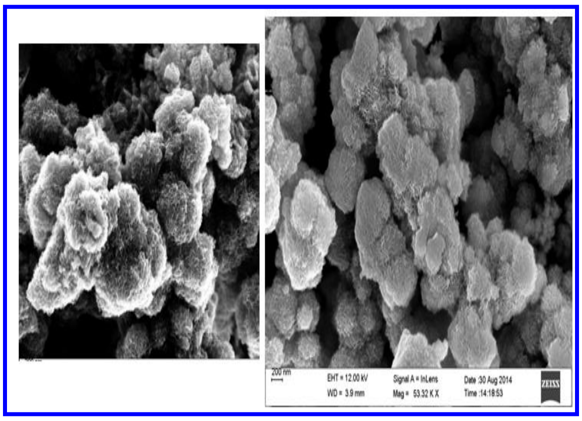

Fig. 3: SEM images of NiSe

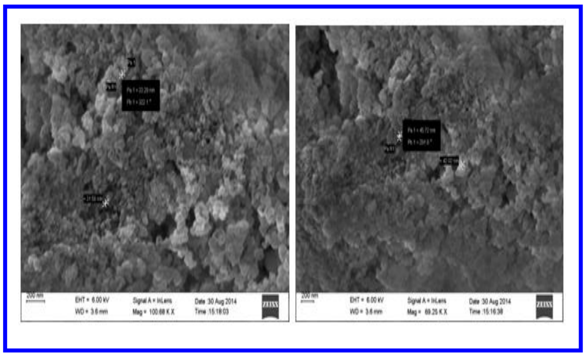

Fig. 4: SEM images of doped NiSe:Cr

Fig.. 5 and 6 shows EDX result of NiSe and NiSe:Cr. EDX is a strong analytical tool for the confirmation of the elements in the sample. EDX fig.. 5 confirms the presence of the elements Ni, Se in NiSe and Fig.. 6 confirms Ni, Se and Cr. Traces of C and O are also found due to atmospheric exposure

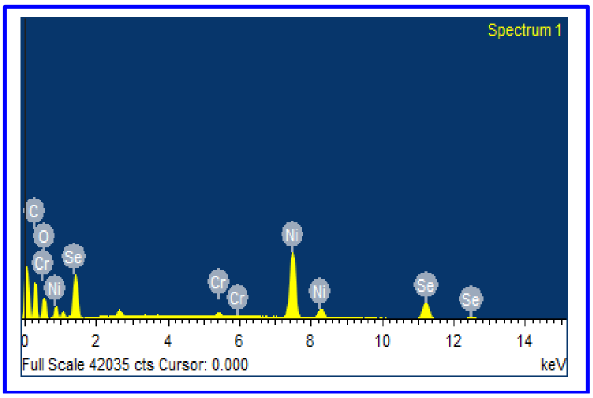

Fig. 5: EDX result of NiSe

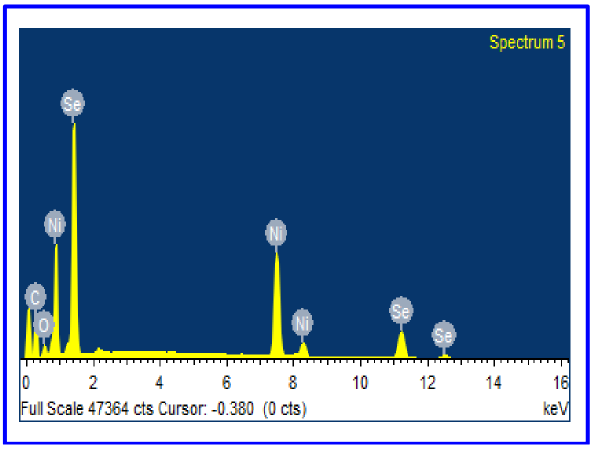

Fig. 6: EDX result of doped NiSe:Cr

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. Fig. 7 and 8 shows PL spectra of NiSe and doped NiSe:Cr.NiSe is a good semiconductor whose conductivity increases on doping with chromium. The

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

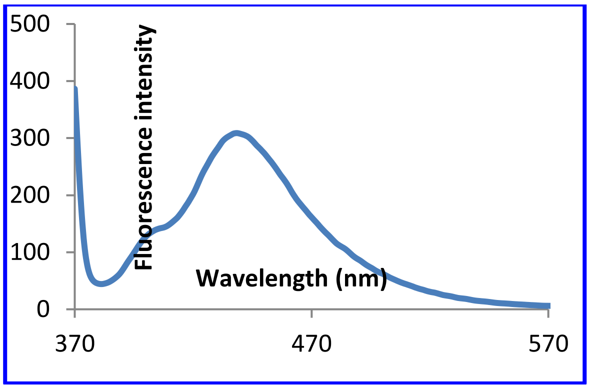

Fig. 7: Solution PL spectra of NiSe

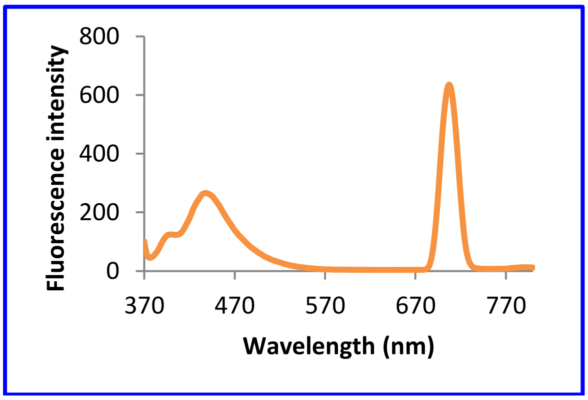

Fig. 8: Solution PL spectra of NiSe:Cr

Fig. 9 and 10 shows absorption spectra of NiSe and doped NiSe:Cr obtained in wavelength range of 200-800 nm. The absorption peak of NiSe is obtained at about 324 nm. It is observed from the absorption spectra of NiSe:Cr that the wavelength of absorption increases on doping. This increase in wavelength shows considerable decrease in ΔE. This also indicates that the conductivity of NiSe increases on doping with Cr. This is also in good agreement with the results obtained from Photo luminescence spectra.

Table 1. Wavelength of Absorption of NiSe

No.	P/V	Wavelength	Abs.
1	↑	324.00	0.212
2	↓	332.00	0.208
3	↓	234.00	0.102

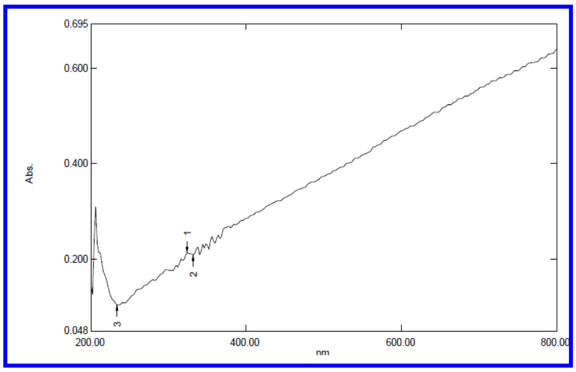

Fig. 9: UV result of NiSe

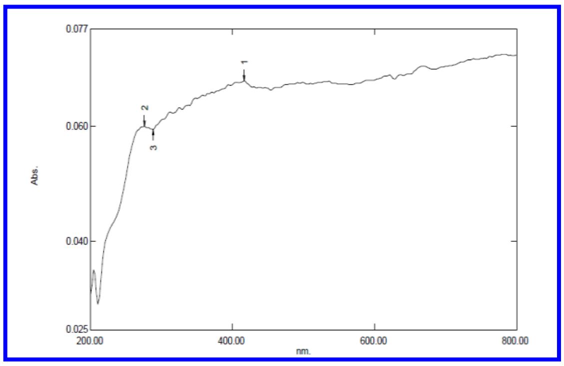

Fig. 10: UV result of NiSe:Cr

Table 2. Absorption wavelength of doped NiSe:Cr

No.	P/V	Wavelength	Abs.
1	↑	416.00	0.068
2	↑	276.00	0.060
3	↓	288.00	0.059

An infrared spectrum represents a fingerprint of a sample with absorption peaks which corresponds 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.

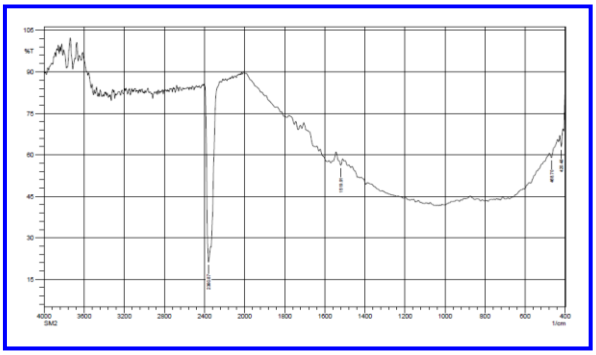

Fig.. 11: FT-IR Result of NiSe

Therefore, infrared spectroscopy can result in a positive identification 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. FT-IR spectra of NiSe and NiSe:Cr is given in fig. 11 and 12.

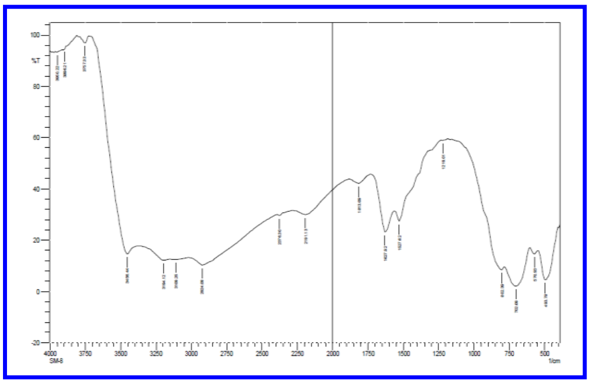

Fig. 12: FT-IR Result of NiSe:Cr

The various absorption peaks and the corresponding vibration modes are as follows.

Table 3. Absorption peaks and the corresponding vibrational modes

NiSe		NiSe:Cr	
γ bond	**Frequency (Cm^{-1})**	**Bond**	**Frequency (Cm^{-1})**
γ Se-H	2360.87	γO-H	3950 - 3109
γC=O	1519.91	γSe-H	2376.30
γNi-O	468.70	γNi-O	702.09
------	------	γCr-O	570 - 493

In fig. 12, the most intense and broadest band appears at 3950 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 fig. 11 and 2376 cm^{-1} in fig. 12 corresponds to the vibrational mode of Se-H bond. The other, much weaker bands appearing between 1527-1813 cm^{-1} can be attributed to C=O bond due to the presence of atmospheric CO_2. 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 700 cm^{-1} can be due to the presence of Ni-O bonds in the powders. The band centered at 570 cm^{-1} is due to vibrational mode of Cr-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.

4. CONCLUSION

NiSe and doped NiSe:Cr were successfully synthesized by simple thermal reduction and co-precipitation process 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 crystalline buster cluster shape after doping with Chromium. The possible reason for the change in the structure was also explained.PL spectra revealed that the conductivity of NiSe is enhanced by doping with Chromium. There is observable increase in absorption wavelength observed in absorption spectra of doped NiSe:Cr.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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