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Study of structural, electrical and optical properties of Nickel doped Tin Selenide crystals

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71.20. Nr – Semiconductor compounds
61.50. ±f – Structure of bulk crystals
78.20. Ci – Optical constants

Abstract –

Nickel doped tin Selenide crystals can be grown by Direct Vapour Transport (DVT) technique. This paper includes structural, electrical and optical characterizations of $\text{SnSeNi}_{0.2}$ crystals done by X-ray diffraction (XRD), Energy dispersive analysis of x-rays (EDAX), surface microstructure topography, Hall Effect measurement carried out to find out type of material, Seeback coefficient and calculation of power factor has been carried out from the data of Thermoelectric Power (TEP) measurements and UV-Visible spectroscopic technique respectively. The optical absorption spectra was obtained in an UV-VIS-NIR spectrometer in the range of 200-2500nm. UV-Visible spectroscopic technique has been used to calculate band gap, the value of band gap was found to be 0.84eV in the visible region. Calculation of various optical parameters has been carried out.

Introduction –

Tin selenide is a narrow band-gap (IV-VI) semiconductor and has received considerable interest for applications including low-cost photovoltaic and memory-switching devices [1, 2]. Here authors have carried out brief study of nickel doped tin Selenide crystals. Aim of this paper is growth and study of structural, electrical and optical properties of $\text{SnSeNi}_{0.2}$ crystals [3-6]. The study of structural, electrical and optical properties is very useful because of large application of such grown crystals in the fabrication of photovoltaic devices. Growth of high-quality crystals with uniform composition is very much important for devices manufacturing. The quality crystal with active epi-layers is used for electronic and optoelectronic applications, this quality directly depends on the chemical homogeneity of the crystal [2]. To improve conducting properties and number of free electrons slight doping of any transition element is necessary. The direct effect of doping can be seen on the band gap values and other structural, electrical and optical properties [1]. The main purpose of this research work is to carry out comparative study of structural, electrical and optical properties of doped Tin Selenide for device fabrication like Photoelectrochemical (PEC) solar cell. The reason behind choosing Ni as a doping material is that the work carries out on Nickel doped Tin Selenide is very less, especially for crystals. According to literature study we found out that Nickel is not a bad conductor for electrical as well as for heat [18-20]. Study of copper doped Tin Selenide has also been carried out. It is well known that copper is better conductor than Nickel but aim of this paper is to study that how doping of material changes the characteristics of Tin Selenide. In addition to this Nickel shows some magnetic properties at

room temperature also which is not reported here. For the study of optical properties it is necessary to have crystals with clean and thin surfaces as well as possible pure and flat surface without any impurities. For the growth of such high quality crystals, Direct Vapour Transport (DVT) technique is very useful [16]. For finding out structural variation and Stoichiometric proportion of elements in the grown crystal, X-ray diffraction and Energy dispersive analysis of x-rays (EDAX) has been carried out, surface micro topography is used to check out flat and pure surface of crystals, data of Hall Effect measurement shows type of material, thermoelectric power (TEP) measurement of grown crystals becomes very useful for calculation of Seeback coefficient and power factor and UV-Visible spectroscopic analysis has been carried out for calculating band gap and various optical parameters.

Experiment –

Starting materials. Sn (99.999%, Chiti chem., Baroda), Se (99.999%, Chiti chem., Baroda) and Ni (99.999%, Chiti chem., Baroda).

Growth. Ingots (10 g) of nominal composition $\text{SnSeNi}_{0.02}$ were synthesized by mixing appropriate ratios of high-purity starting materials (Sn, Se and Ni) in quartz tubes. The tubes were evacuated to a pressure of $\sim 10^{-5}$ torr, flame-sealed, slowly heated to 1000K at hot zone part and 950K at growth zone part of furnace in 12 h, hold at this temperature for 8 h and subsequently furnace cooled to room temperature. The obtained ingots were crushed into powder and placed in a quartz tube, evacuated and flame-sealed, then this tube slowly heated to 1,273K (Hot zone) in the steps of 10K/hour in 128h, shocked at this temperature for 96h and subsequently furnace cooled to room temperature. The temperature of growth zone was kept 50K lesser than hot zone. SnSe crystals with

dimensions of 10mm (diameter) $\times$ 15mm (length) were obtained. Good experimental repeatability was evidenced by crystals with high qualities like showing shining flat surfaces, no cracks or obvious defects, and no porosity or other macroscopic features. [1]

Characterization techniques. Rigaku Ultima IV recorded the X-ray powder diffractogram by using $\text{CuK}\alpha$ radiation. For this purpose, many small crystals from each group were finely ground with the help of agate mortar and filtered through 106-micron sieve to obtain grains of nearly equal size. It is very important to find Stoichiometric proportion of elements in the formed compound especially when doping entered into picture. For this Stoichiometric characterization Energy dispersive analysis of x-rays (EDAX) is used. The surface microstructures of the fresh as-grown faces of crystals were examined under 'Epignost' optical microscope (Carl Zeiss Jena GmbH, West Germany). A study of microstructure of the as grown crystals of $\text{SnSeNi}_{0.2}$ by DVT technique is presented here. Morphological study of grown surfaces of bulk crystal consists of a variety of structures whose study leads to derive the condition and mechanism of growth. The optical absorption data were taken by means of (Perkin Elmer Model: Lambda- 19) Spectrophotometer. The surfaces of this type of grown crystals were mirror like. Crystal flakes were pasted on a thick black paper with a cut exposing the crystal flake to the incident light. The reference used for this work was a replica of the black paper, having the cut in the exactly the same position as the crystal flake. This arrangement was necessary because the crystal size was smaller than that of the sample compartment. In this present case, absorption spectrum taken over the spectral range 200-2500 nm. The absorption coefficient ' α ' was determined at every step of 5 nm and had scanning speed 240 nm/min.

Result. –

Structural studies X-ray diffractogram (XRD). The typical XRD diffraction peaks are shown in Figure 1. The diffraction peaks in the XRD pattern clearly shows the crystalline nature with reflection planes corresponding to (111), (400), (311), (020), (202), (600), (420), (620) and (820). The values of lattice parameters ' a ', ' b ' and ' c ', unit cell volume and X-ray density obtained from the diffractogram of grown crystals as shown in Table 1. From the values of lattice parameters and c/a ratio it is clear that grown crystal possesses FCC orthorhombic crystal structure. The value of c/a ratio indicates the presence of compressive strain and the average crystal size calculated after appropriate background correction from X-ray line broadening, the line broadening arises due to strain or imperfection in the crystals. Scherrer [7] first observed that small crystallite size could give rise to line broadening. He derived a well known equation for relating the crystallite size to the broadening, which is known as Scherrer formula. The average crystal size (D) of the samples is calculated for the diffraction plane (400) using Debye Scherrer's formula [7].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Where λ is the wave length of X-ray used (1.5405 Å), β is the angular peak width at half maximum in radian along (400) plane, and θ is Bragg's diffraction angle.

Fig.1: XRD pattern of grown crystal

Rietveld refinement A Rietveld structure refinement has been done for X-ray powder diffraction data of $\text{SnSeNi}_{0.2}$ which is shown in Figure 1(a).

Fig.1(a): Rietveld refinement of X-ray powder diffraction data of $\text{SnSeNi}_{0.2}$

The Rietveld refinement and synthesis experiment described here forms part of a large study [21-23]. The raw diffraction pattern was prepared for Rietveld refinement using the **General Scattering Analysis Software (GSAS)** [27]. The background was fitted with a polynomial curve; an overall scale factor was also used. An asymmetric pseudo-voigt line shape was employed. The arrangement between the observed and calculated profiles in the Rietveld differences plot is illustrated in Figure 1. Good agreement factors ($R_{\text{fact}} = 21.305\%$, $R_{w, \text{fact}} = 24.537\%$, $\chi^2 = 3.1$, $R_{\text{ex}} = 13.917\%$) were reached, as illustrated in the Rietveld plot included in Figure 1(a).

The micro-strain (ϵ) can be calculated using the formula [8],

$$\epsilon = \frac{\beta \cos \theta}{4} \quad (2)$$

Table 1. Values of lattice parameters and c/a ratio for grown crystal

a (Å°)	b (Å°)	c (Å°)	c/a ratio
11.506	4.159	4.4523	3.869

Table 2. Values of unit cell volume, average crystal size (D) and microstrain (ϵ) of grown crystal.

Unit cell volume (Å°) ³	Average crystalline size (μm)	Microstrain $\epsilon \times 10^{-4}$ (lin ⁻² m ⁻⁴)
213.07	82.875	4.37

By comparing the values of lattice parameter of nickel doped Tin Selenide with the data of pure Tin Selenide, effect of nickel doping can be clearly seen. Doping of nickel slightly increases the lattice parameters [$a=11.500 \text{ \AA}$, $b=4.150 \text{ \AA}$, $c=4.453 \text{ \AA}$], unit cell volume [$212.75 (\text{ \AA})^3$] and average crystalline size [$79.072 \mu\text{m}$] in comparison to pure Tin Selenide. According to literature study the ionic radii of Sn, Se and Ni atom is 145 pm, 115 pm and 135pm respectively. It might be possible that Ni replaces Sn, because the ionic radius of Ni is less than that of Sn [18-20].

Energy dispersive analysis of x-rays (EDAX).EDAX is used to analyse the amount of nickel in tin selenide. The chemical compositional analysis of grown crystals has been carried out by EDAX. The typical EDAX spectrum of grown crystals is shown in Figure 2. The addition of nickel induces a dominant effect on the structural, electrical and optical properties.

Fig. 2: Energy dispersive analysis X-ray (EDAX) of grown crystals at room temperature

The EDAX analysis confirms the presence of nickel in the Tin Selenide system and wt. % is very nearly equal to their nominal stoichiometry within the experimental error. Therefore, the EDAX spectra show well agreement with the experimental concentration used for $\text{SnSeNi}_{0.2}$. Experimentally calculated and data got from EDAX spectra are shown in Table 3.

Table 3: Chemical composition of grown crystals by EDAX analysis

Wt% of element Obtained by EDAX		
Sn	Se	Ni
56.68±0.13	37.68±0.10	5.59±0.17

Surface-microtopography. Microtopography [Figure 3 (a)] indicates the flat surface of as grown crystals. Figure 3 (b-d) indicates that the growth of crystals promoted by lateral spreading of layers. Moreover the irregular shape of growth layers at the edges of smooth flat faces indicates that the growth was rapid [9]. In the case of $\text{SnSeNi}_{0.2}$ growth spirals are observed on the surface of crystals as shown in Figure 3(b-d). Figure 3(b-d) indicates that growth was driven by a screw dislocation mechanism. In growth from vapour, theory predicts that the growth of a crystal surface with steps will be the result of three processes: (1) transport of molecule from vapour to surface of solid, (2) diffusion of adsorbed molecule to steps, and (3) diffusion of molecules along the edge of a step to a kink. [10, 11]

Fig.3 (a-d): The surface microstructure on the face of grown crystals

Thermoelectric power (TEP) measurements. Measurement of thermoelectric power as a function of temperature is one of the important method for investigating electronic properties of solids. The thermoelectric power (S) provides useful information about the mechanism of electrical transport. For the thermoelectric power (TEP) measurements, crystals having dimensions of $10 \times 5 \times 0.04 \text{ mm}^3$ were used. The TEP measurements were carried out by using the thermopower set-up developed by Scientific Solutions, Mumbai. This experimental set-up consists of two blocks: (i) Sample holder with heaters and pick up probes. (ii) Electronic circuits controlling temperature and temperature gradient across the sample. The sample holder consists of two low power heaters A and B (15 each). The temperature (T) of the heaters A and B is measured by thermocouple and the temperature gradient between A and B is measured by differential temperature sensor [25-26].

Fig.4: The variation of thermoelectric power with thousand inverse of temperature for grown crystals

As pointed out, the quantity S can be used to determine the mobility ratio, the concentration of carriers, the position of dominant carriers or the type of dominant electronic conduction. Fermi level etc. in addition, the sign of S indicated the type of crystals. For the study of temperature dependent thermoelectric power ‘S’ of a n-type semiconductor, the following expression can be used.

$$S = \frac{k}{e} \left[A + \frac{E_F}{kT} \right] \tag{3}$$

Where k is Boltzmann constant, e is the electronic charge, A is the constant determined by the dominant scattering process and E_F is the separation of the Fermi level, from the top of the

valance band. [12] The Seebeck coefficient is not the only number that determines the usefulness of a material in a thermoelectric generator or a thermoelectric cooler. The Seebeck coefficient can be calculated as the ratio of voltage produced due to temperature difference along surfaces of crystals in the temperature range from 303 to 538 K. The Seebeck coefficient shows almost isotropic behavior. Under a given temperature difference, the ability of a material to produce useful electrical power is determined by its power factor ($S^2\sigma$). The electrical behavior involves a reversible phase transition from low temperature $Pnma$ space group to high temperature $Cmcm$ space group [1]. Variation power factor with temperature is illustrated in Figure 5. The value of power factor increases with increase in temperature. The sign of thermoelectric power (TEP) in the semiconducting phase decide the type of majority charge carriers. The n-type nature of the samples supports the conclusions drawn from the Hall Effect measurement. Evaluated values of Fermi energy, effective mass and scattering parameter are listed in Table 4. The fact that TEP in grown crystal is negative clearly indicates that these crystals are n-type semiconductor. Further in all cases there is no change in sign of TEP with an increase in temperature. This suggests that a material does not undergo any phase transition in the entire temperature range studied.

Fig. 5: Variation of power factor with thousand inverse of temperature for grown crystals

Table 4: Evaluated values of Fermi energy, effective mass and scattering parameter for grown crystals

Parameters	SnSe	SnSeNi _{0.2}
Fermi Energy E_F (eV)	0.154	0.176
Effective mass m_e^* (kg)	0.295 m_0	0.319 m_0
Scattering Parameter s	2.480	2.459

Optical study. The optical properties of crystals such as IV-VI compound are governed by the interaction between the crystal and the electric field of the electromagnetic wave. Various types of transitions give rise to different wavelength dependencies of the absorption coefficient near the fundamental absorption edge. From the data of absorption coefficient (α), UV-Visible spectroscopic technique has been used to calculate band gap, Absorption (α), Transmission (T), Reflection (R), Extinction Coefficient (k), Refractive Index (η), Real part of Dielectric constant (ϵ_r), Imaginary part of Dielectric constant (ϵ_i) and Optical Conductivity (σ). All these parameters have been calculated by using these equations (Equation 4 and 5). The dependence of absorption coefficient ' α ' in terms of direct and indirect transitions can be performed with the help of Tauc relation (Equation 4 and 5)

$$\alpha h\nu = A(h\nu - E_g)^r \quad (4)$$

$$\alpha h\nu = \sum_j B_j (h\nu - E'_g \pm E_{pj})^r \quad (5)$$

where ' α ' is the absorption coefficient, $h\nu$ is the energy of the incident photon, E_g the energy of photon for the direct transition, E'_g the energy for indirect transition. A and B are parameters depending on the temperature [13, 14]. Optical absorption spectrum for grown crystals is shown in Figure 4. A graph was plotted between $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for the determination of direct energy band gap of grown crystal as shown in Figure 6 straight line was obtained. The extrapolation of the straight line gives the value of the direct band gap of this sample shown in Figure 6 and its value is 0.84eV. The effect of nickel doping also seen here in pure Tin Selenide crystal sample the direct band gap value is about 0.84eV. The isotropic behavior of Seebeck coefficient has been consistent with electronic band structure calculations, which shows the variation of band gap.

Fig. 6: The plot of $(\alpha h\nu)^{1/2}$ versus photon energy of grown crystal

One of the most important optical constants of a material is its refractive index, which in general depends on the wavelength of the electromagnetic wave, through a relationship called *dispersion*. In materials where an electromagnetic wave can lose its energy during its propagation, the refractive index becomes complex. The real part is usually the refractive index, η , and the imaginary part is called the *extinction coefficient*, K . The refractive index can be calculated as,

$$\eta = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \quad (6)$$

Where R = Reflection

Extrinsic coefficient can be calculated as,

$$K = \frac{\alpha \lambda}{4\pi} \quad (7)$$

Where α =Absorption coefficient, λ = Wavelength

It is observed that the value of extrinsic coefficient decreases when wavelength increases. ϵ_r is the static dielectric constant or relative permittivity. As ϵ_r depends on the wavelength of light, the refractive index η also depends on the wavelength of light, and this dependence is called *dispersion*. In addition to dispersion, an electromagnetic wave propagating through a lossy medium experiences attenuation, which means it loses its energy, due to various loss mechanisms such as the generation of phonons (lattice waves), photo generation, free carrier absorption, scattering, etc. The complex dielectric constant is a fundamental intrinsic property of materials

directly linked to its refractive index. The real part of the dielectric constant ϵ_r is linked to the electronic polarizability whereas the imaginary part ϵ_i is related to the absorption phenomenon due to dipole motion [15]. Real dielectric constant can be calculated as,

$$\epsilon_r = \eta^2 - K^2 \quad (8)$$

Imaginary part of dielectric constant can be calculated as,

$$\epsilon_i = 2\eta K \quad (9)$$

Fig. 7: The plot of refractive index (η) and extrinsic coefficient (K) versus wavelength for grown crystal

The two relations Equation 8 is relation between dielectric constant and the refractive index, and Equation 9 point out the relation between dielectric constant and the extinction coefficient, with an inter-dependence of these factors, which is quadratic and linear for the real and imaginary parts, respectively. The dependence of ϵ_r and ϵ_i on wavelength calculated with the parameter values of the $\text{SnSeNi}_{0.2}$ obtained during our experiments is shown in Figure 8.

As seen in Fig. 8, ϵ_r increases sharply in the wavelength range between 200 nm and 650 nm and decreases slowly after this region, whereas ϵ_i increases slowly for shorter wavelengths under wavelength value corresponding to $K < 500$ nm but decreases above this threshold. It contrasts that the variation of ϵ_r mainly depends on the refractive index due to the small value of K^2 compared with the value of η^2 (Equation 8), while ϵ_i is mainly influenced by K , showing its dependence to the absorption coefficient [15].

Fig. 8: The plot of real and imaginary part of dielectric constant (ϵ_r , ϵ_i) versus photon energy for grown crystals

Optical response of a material is mainly studied in terms of the optical conductivity (σ). Optical conductivity can be calculated as,

$$\sigma = \frac{\alpha \eta c}{4\pi} \quad (11)$$

Where α =Absorption coefficient, η = Refractive index of material, c = velocity of light in medium

Conclusion. –

Author has successfully grown $\text{SnSeNi}_{0.2}$ single crystals using direct vapor transport (DVT) technique. XRD measurement reveals the orthorhombic crystal structure of $\text{SnSeNi}_{0.2}$ crystal and its crystalline nature. The value of lattice parameters a , b , and c , unit cell volume and densities is listed in Table 2 by characterizing crystals by X- rays. EDAX measurement indicated that nickel is really doped. From thermodynamic power measurement n - type behaviour of $\text{SnSeNi}_{0.2}$ can be shown. We concluded from the presented work, that $\text{SnSeNi}_{0.2}$ crystals grown by direct vapour transport method certainly leads to semiconducting behaviour of transport properties with increasing the temperature. We conclude that it is n - type semiconductor with detailed report. The analysis of the optical absorption in $\text{SnSeNi}_{0.2}$ crystals near the absorption edge has shown that direct transition takes place in these compounds. The tunability of the bandgap allows for the fabrication of PECs cells and phototransistors using such crystals as their bandgap is falling within the visible range of electromagnetic spectrum.

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