EXPERIMENTAL STUDY OF STRUCTURAL, VIBRATIONAL AND OPTICAL BAND GAP OF NICKEL DOPED TIN OXIDE

Zin Bo Htut[1], Myo Paing Htwe[2], Win Kyaw[3] and Soe Soe Nwe[4]

Abstract

Undoped Tin Oxide (SnO_2) and Nickel doped Tin Oxide, $Sn_{0.5}Ni_{0.5}O_2$ were prepared by chemical co-precipitation method. Analytical Reagent grade Stannous Chloride Double-hydrate ($SnCl_2.2H_2O$) and Nickel Chloride Hexahydrate ($NiCl_2.6H_2O$) were used to prepare the desired materials. De-ionized (DI) water is used as the solvent to prepare saturated solutions. Aqueous Ammonia is used as an agent material. The co-precipitated $SnO_2$and $Sn_{0.5}Ni_{0.5}O_2$were annealed at 350°C for 2 h. The samples were characterized by X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR) and Ultra-Violet Visible-Near Infrared (UV-VIS-NIR) spectroscopy to study the structural, vibrational and optical properties of the samples. XRD patterns showed that the samples analogous to tetragonal structure. The broadening of observed spectral lines indicated the fine particle nature. FTIR spectra confirmed the existence of the sample phase. Optical energy band gaps were determined from $(\alpha h\upsilon)^2$ vs. hυ graphs by using UV-VIS-NIR transmission spectra.

Keywords: SnO_2, $Sn_{0.5}Ni_{0.5}O_2$, co-precipitation method, XRD, FTIR, UV-VIS-NIR.

Introduction

Tin Oxide (SnO_2) is an important material due to its properties such as high degree of transparency in the visible spectrum, strong physical and chemical interaction with adsorbed species, low operating temperature and strong thermal stability in air (up to 500°C) [Azurdia,(2006)].It is an n-type semiconductor with a large band gap(3.6 eV at the room temperature), which can be used in gas sensor, solar cells, glass electrodes and secondary lithium batteries [Julian, (2003)].

A number of attempts have been made by developing effective synthetic techniques in the preparation of metal ions-doped SnO nanoparticles, such as sol-gel, co-precipitation [Khan,(2015)] and chemical vapor deposition [Liu,(2015)]. In this work, undoped SnO_2 and Ni-doped SnO_2 nanoparticles were prepared by chemical co-precipitation method and structural, vibrational and optical characteristics of the as-prepared samples were studied by XRD, FTIR and UV-VIS-NIR spectroscopy.

Experimental Details

Preparation of Samples

Undoped Tin Oxide, SnO_2 and Nickel doped Tin Oxide, $Sn_{0.5}Ni_{0.5}O_2$ were prepared by chemical co-precipitation method. For the preparation of undoped Tin Oxide, SnO_2 sample, the starting materials of Analytical Reagent (AR) grade Tin Chloride Double-hydrate ($SnCl_2.2H_2O$) was used and the Ammonia solution was used as an agent. Also for the preparation of Nickel doped Tin Oxide, $Sn_{0.5}Ni_{0.5}O_2$ sample, Tin Chloride Double-hydrate ($SnCl_2.2H_2O$) and Nickel Chloride Double-hydrate ($NiCl_2.2H_2O$) were used as the starting materials. Flow diagrams of the sample preparation procedure of undoped SnO_2 and $Sn_{0.5}Ni_{0.5}O_2$are shown in Figure 1(a) and (b).

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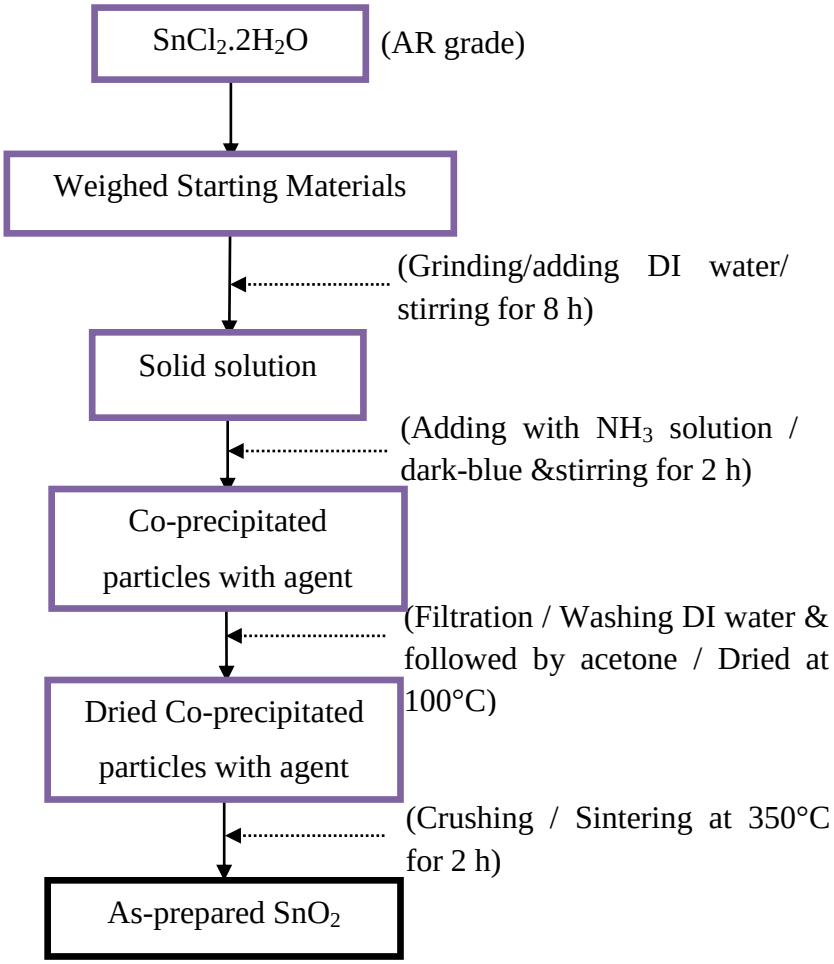

Figure 1 (a) Flow diagram of undoped SnO_2 sample preparation

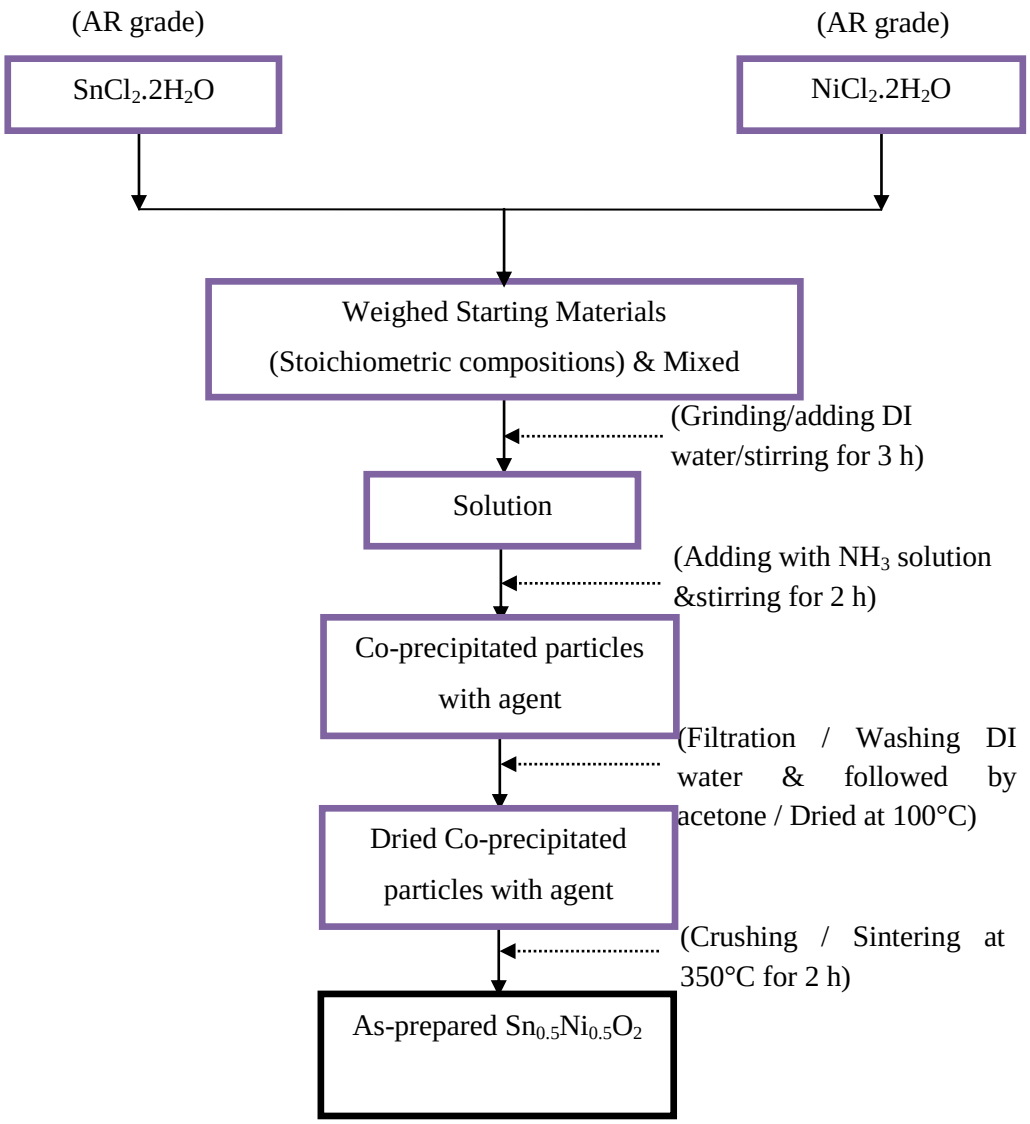

Figure 1(b) Flow diagram of $Sn_{0.5}Ni_{0.5}O_2$ sample preparation

XRD, FTIR and UV-VIS-NIR Measurements

Phase formation, structure analysis, the lattice parameters evaluation and crystallite sizes estimation of Nickel doped Tin Oxide, $Sn_{0.5}Ni_{0.5}O_2$ and undoped Tin Oxide, SnO_2samples were investigated by PC-controlled RIGAKU MULTIFLEX X-ray Diffractometer [Universities' Research Centre (URC), University of Yangon] using Ni-filter with CuK_α radiation, λ = 1.54056 Å. Vibrational characteristics and mode assignments of the samples were studied by Fourier Transform Infrared (FTIR) spectroscopy. FTIR transmission spectra were observed by PC-controlled SHIMADZU FTIR-8400 Spectrophotometer [Universities' Research Centre (URC), University of Yangon]. Optical transmission and energy band gaps were determined by using Ultraviolet-Visible-Near Infrared (UV-VIS-NIR) spectroscopy. UV-VIS-NIR transmission spectra were collected on PC-controlled UV-1800 Spectrophotometer.

Results and Discussion

Structural Investigation

Powder XRD patterns of Nickel doped Tin Oxide, $Sn_{0.5}Ni_{0.5}O_2$ and undoped Tin Oxide, SnO_2samples are shown in Figure 2(a) and (b). To assign the observed XRD lines, the collected spectral lines were identified by using standard JCPDS data library files of

(i) Cat. No. 77-0447>Cassiterite, syn - SnO_2 and Cat. No. 89-7130>Bunsenite, syn - NiO for theNickel doped Tin Oxide, $Sn_{0.5}Ni_{0.5}O_2$ sample and

(ii) Cat. No. 99-0024>SnO_2 – Cassiterite for undoped Tin Oxide, SnO_2sample.

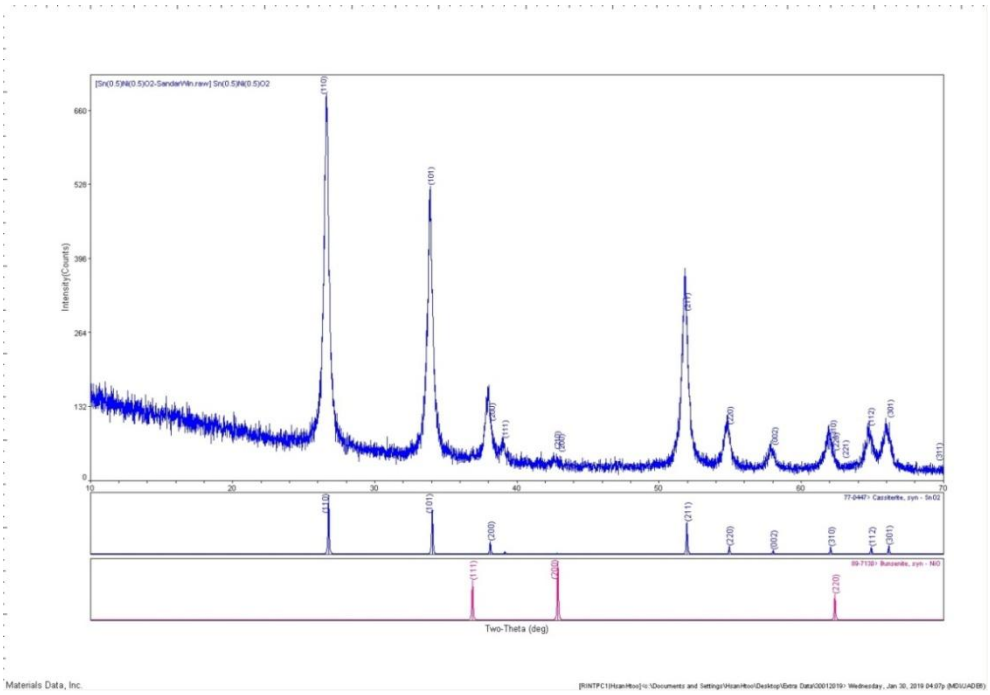

Figure 2 (a) XRD pattern of $Sn_{0.5}Ni_{0.5}O_2$

The observed diffraction lines are found to be mostly agreed with standard JCPDS and it indicates the $Sn_{0.5}Ni_{0.5}O_2$and undoped SnO_2 samples belong to tetragonal structure. The lattice parameters are evaluated by using crystal utility of the equation, $\frac{1}{d^2}=\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2}=\frac{4\sin^2\theta}{\lambda^2}$, where (hkl) is the Miller indices, "d' is the atomic spacing (Å) and "*a* and *c*" are the lattice parameters (Å). The lattice parameters are obtained as a = b = 4.66 Å and c = 3.15 Åfor $Sn_{0.5}Ni_{0.5}O_2$and a = b = 4.74 Å and c = 3.20 Åfor SnO_2.

The crystallite sizes of the samples were estimated by using the Scherrer formula,

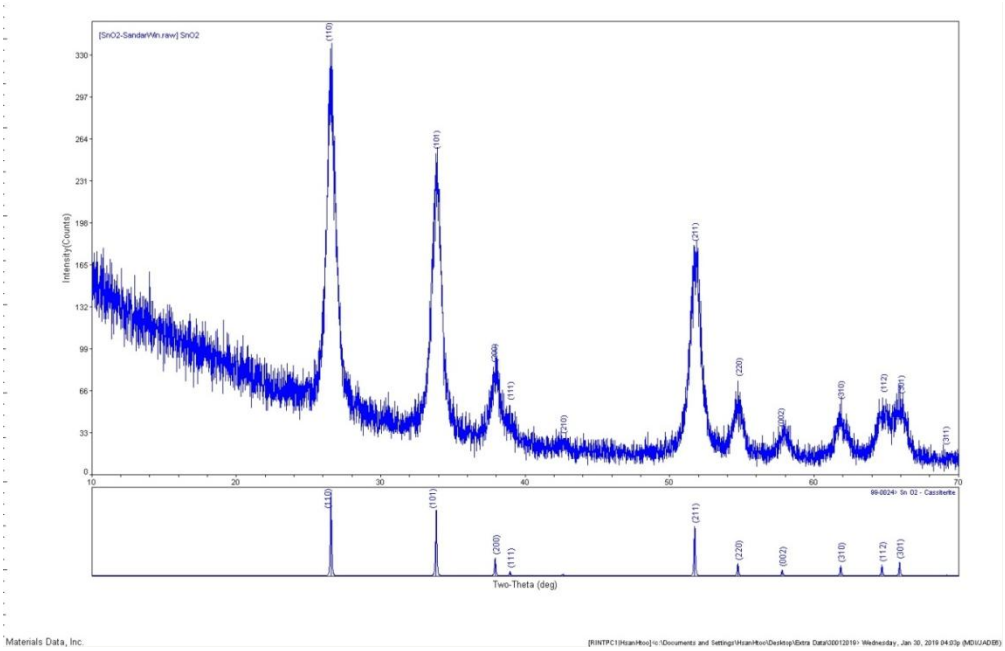

Figure 2 (b) XRD pattern of SnO_2

$D=\frac{0.9\lambda}{B\cos\theta}$,where "*D*" is the crystallite size (nm), "λ' is the wavelength of incident X-ray (Å), "θ" is the diffraction angle of the peak under consideration at FWHM (°) and "B" is the observed FWHM (radians). The crystallite sizes are obtained as 33.82 nm for $Sn_{0.5}Ni_{0.5}O_2$and 27.74 nm for SnO_2. It was found that the crystallite sizes of the samples varied with the dopant effects of Ni on Sn. The obtained crystallite sizes indicate the nanosized nanocrystalline materials and the samples are the very fine particle nature.

Vibrational Analysis

According to the molecular vibrational theory, a diatomic molecule has two types of normal vibrations: (i) transverse-optical and (ii) longitudinal-optical vibrations and also a non-linear tri-atomic molecule such as SnO_2 and $(Sn_{0.5}Ni_{0.5})O_2$ has three types of molecular vibrations: (i) υ_1-mode (symmetric-stretching), (ii) υ_2-mode (bending) and (iii) υ_3-mode (asymmetric-stretching) respectively.

In the present work, FTIR transmission spectra of Nickel doped Tin Oxide, $Sn_{0.5}Ni_{0.5}O_2$ and undoped Tin Oxide, SnO_2samples are shown in Figure 3(a) and (b). The observed wavenumbers corresponding vibrational characteristics of the samples are tabulated in Table 1(a) and (b). The observed wavenumbers of the $Sn_{0.5}Ni_{0.5}O_2$ and $SnO_2$are found to be clearly shifted due to crystalline environments.

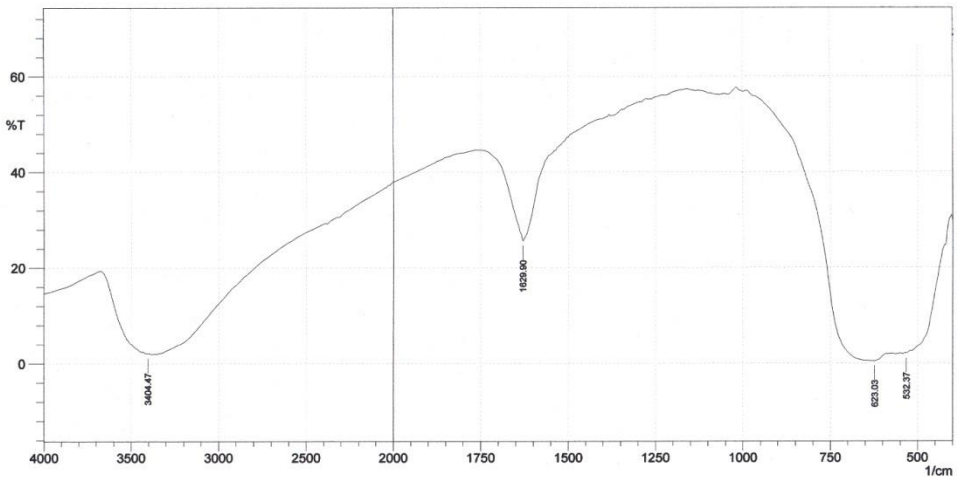

Figure 3 (a) FTIR spectrum of $Sn_{0.5}Ni_{0.5}O_2$

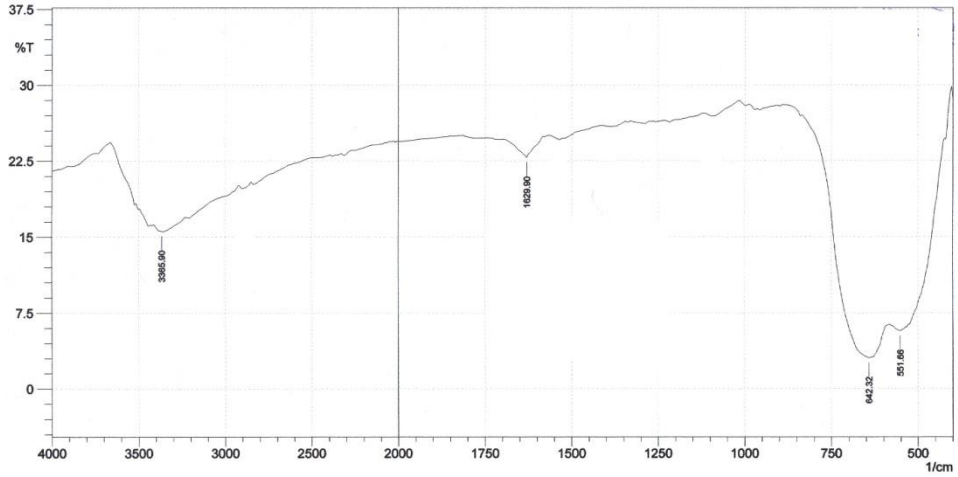

Figure 3 (b) FTIR spectrum of SnO_2

The lines at 1630 cm^{-1} and 3404 cm^{-1}in Figure 3(a) and the lines at 1630 cm^{-1} and 3366 cm^{-1}in Figure 3(b) indicate the (υ_2-mode) bending vibration of H_2O molecules and (υ_3-mode) asymmetric-stretching vibration of H_2O molecules. These lines appear in FTIR spectra of KBr pellet method due to the distribution of moisture in the surrounding of FTIR spectrophotometer.

Table 1 (a) Wavenumbers and corresponding vibrational characteristics of $Sn_{0.5}Ni_{0.5}O_2$

Wavenumbers (cm^{-1})	**Vibrational characteristics**	**Molecules**
532	υ_{TO}-stretching	$Sn_{0.5}Ni_{0.5}O_2$
623	υ_{TO}-stretching	$Sn_{0.5}Ni_{0.5}O_2$
1630	υ_2-bending	H_2O
3404	υ_3-asymmetric stretching	H_2O

Table 1 (b) Wavenumbers and corresponding vibrational characteristics of SnO_2

Wavenumbers (cm^{-1})	Vibrational characteristics	Molecules
552	υ_{TO}-stretching	SnO_2
642	υ_{TO}-stretching	SnO_2
1630	υ_2-bending	H_2O
3366	υ_3-asymmetric stretching	H_2O

UV-VIS-NIR Analysis

To determine the optical band energies of the Nickel doped Tin Oxide, $Sn_{0.5}Ni_{0.5}O_2$ and undoped Tin Oxide, SnO_2samples, UV-VIS-NIR transmission spectra were observed. UV-VIS-NIR transmission spectra are shown in Figure 4(a) and (b). The spectra show that the samples demonstrate that less than 100% transmittance of throughout the spectrum. The theory of optical transmission gives the relationship between the absorption coefficient "α" and the photon energy "hν' has a relation; α = -ln (1/T). Plots of the variation of $(\alpha h\nu)^2$ versus hν graphs are shown in Figure 5(a) and (b). The optical band gap "E_g" can be obtained by using the extrapolating the interception of the highest and linear portion of $(\alpha h\nu)^2$-hν curve on hν (energy) axis. The optical band gaps of the $Sn_{0.5}Ni_{0.5}O_2$ and SnO_2samples are obtained as 3.9 eV and 3.6 eV respectively.

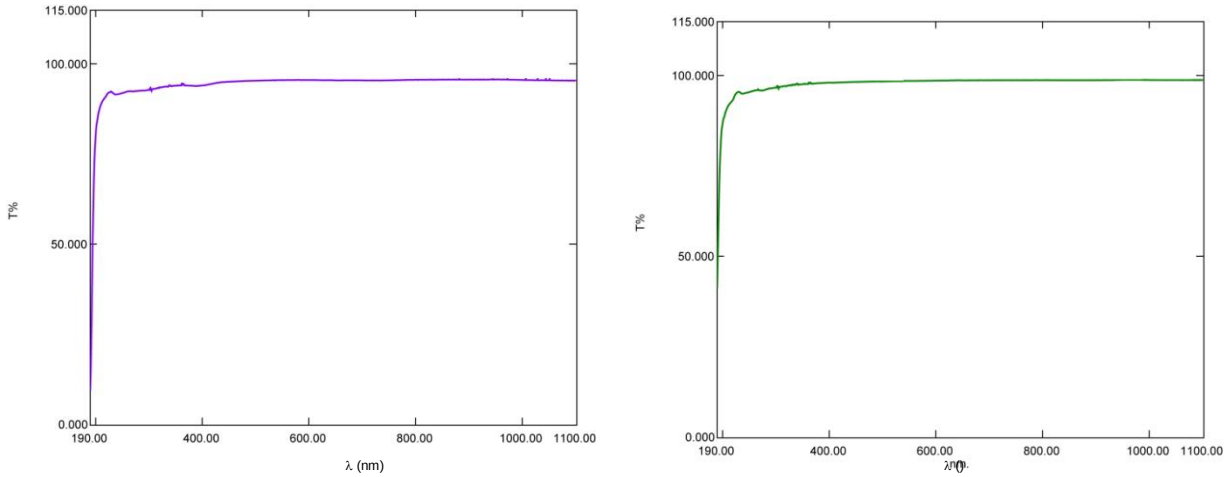

Figure 4 UV-VIS-NIR transmission spectra of (a) $Sn0.5Ni_{0.5}O_2$ and (b) SnO_2

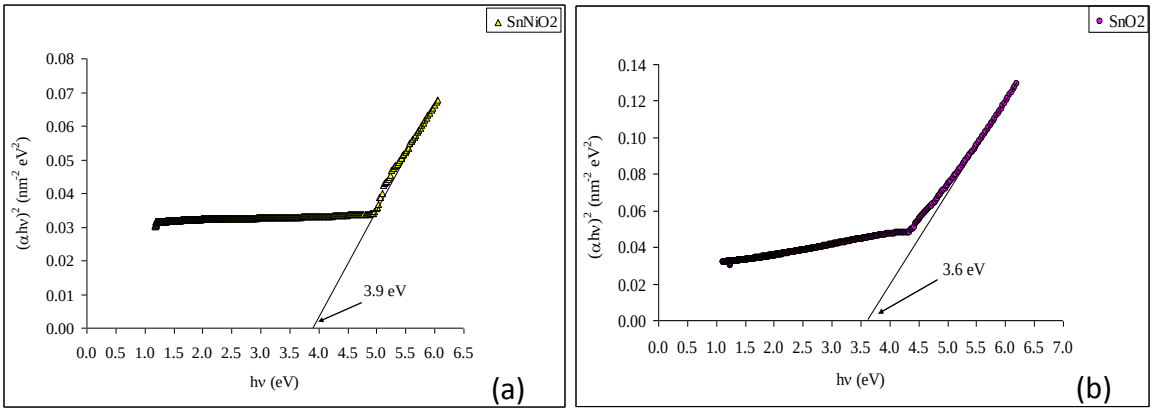

Figure 5 Plots of $(\alpha h\upsilon)^2$ versus hυ graphs of (a) $Sn_{0.5}Ni_{0.5}O_2$ and (b) SnO_2

Conclusion

Undoped Tin Oxide, SnO_2 and Nickel doped Tin Oxide, $Sn_{0.5}Ni_{0.5}O_2$ were prepared by chemical co-precipitation method. Structural, vibrational and optical characteristics were reported in this work. XRD patterns reveal that the samples analogous to tetragonal structure. The lattice parameters are obtained as a = b = 4.66 Å and c = 3.15 Å for $Sn_{0.5}Ni_{0.5}O_2$and a = b = 4.74 Å and c = 3.20 Å for SnO_2. The crystallite sizes are obtained as 33.82 nm for $Sn_{0.5}Ni_{0.5}O_2$and 27.74 nm for SnO_2. It was found that the lattice parameters and the crystallite sizes of the samples varied with the dopant effects of Ni on Sn. FTIR spectra showed the vibrational characteristics of the samples. The observed wavenumbers were found to be shifted due to the dopant effects of Ni on Sn. UV-VIS-NIR transmission spectra showed that the samples demonstrate that less than 100% transmittance of throughout the spectrum. The optical energy band gaps of the $Sn_{0.5}Ni_{0.5}O_2$ and SnO_2samples were obtained as 3.9 eV and 3.6 eV respectively.

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