Optical Characteristics of Nickel Substituted Cobalt-Zinc Ferrites Studied by UV-VIS-NIR Spectroscopy

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Abstract

Nickel substituted Cobalt-Zinc ferrites with the general formula $Co_{0.5-x}Ni_xZn_{0.5}Fe_2O_4$ (where x = 0, 0.1, 0.2, 0.3) were prepared by chemical co-precipitation method and annealed at 600°C for 2 hours. All the ferrite samples have been characterized by using UV-VIS-NIR (Ultraviolet-Visible-Near Infrared) spectroscopy. Optical transmittance of UV-VIS-NIR radiation passed through the sample and the optical energy band gap were examined. Optical transmittance and energy band gap (E_g) of the crystal were determined from T% - λ and $(\alpha h\nu)^2$ – hν relationships. It was found that the energy band gap decreases with increase in concentration of Ni.

Keywords: Nickel substituted Cobalt-Zinc ferrites, co-precipitation method, UV-VIS-NIR, Optical transmittance, optical energy band gap

Introduction

Magnetic materials are gaining importance because of their wide range of applications in high-density magnetic recording (Adam et al., 2009), medicine (Ahmad & Farid, 2012), sensors and actuators (Attia, 2006). Due to their large resistivities; ferrites are of great importance as high-frequency magnetic materials (Fawzi et al., 2010). Their physical properties depend on several factors among of them are, method of preparation, chemical composition, sintering temperature, and distribution of cations among tetrahedral and octahedral sites (Joshi, 2003; Paduraru et al., 2003; Rani et al., 2013). Spinel-type oxides (MFe_2O_4 where M is a divalent metal), which include the magnetic ferrites, are often denoted by the formula AB_2O_4 where A and B refer to tetrahedral and octahedral sites, respectively, in the fcc oxygen lattice (Rani et al., 2013; Sathishkumar et al., 2010).

UV-VIS-NIR (Ultraviolet-Visible-Near Infrared) is the spectroscopy, probes the electronic transitions of molecules that absorb light in the Ultraviolet, Visible and Near Infrared region of the electromagnetic spectrum is considered a reliable and accurate analytical technique for the qualitative as well as the quantitative analysis of the samples. When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption (intensity) at each wavelength. The resulting spectrum is presented as a graph of absorbance versus wavelength (Sonal Sighal et al., 2011). The present work deals with the preparation of $Co_{0.5-x}Ni_xZn_{0.5}Fe_2O_4$ (where x = 0, 0.1, 0.2, 0.3) ferrites using chemical co-precipitation method and their optical properties have been studied by UV-VIS-NIR spectroscopy.

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Experiment

Preparation of Nickel substituted Cobalt-Zinc ferrites

Nickel substituted Cobalt-Zincferrites with the formula $Co_{0.5-x}Ni_xZn_{0.5}Fe_2O_4$ (where x= 0, 0.1, 0.2, 0.3) were prepared by co-precipitation method. Aqueous solutions of Analar (AR) grade Nickel Chloride Hexahydrate $(NiCl_2.6H_2O)$, Zinc Sulphate Heptahydrate $(ZnSO_4.7H_2O)$, Cobalt Chloride Hexahydrate $(CoCl_2.6H_2O)$ and anhydrous Ferric Chloride $(FeCl_3)$ with the respective stoichiometry were mixed thoroughly and stirred at 80°C using a magnetic-stirrer. It was then transferred immediately into a boiling solution of NaOH under stirring throughout the reaction. Conversion of metal salts into hydroxides and subsequent transformation of metal hydroxide into ferrites took place upon 100°C and maintained for 1 h until the reaction was complete. The ferrites thus formed were isolated by centrifugation and washed four times with de-ionized (DI) water followed by acetone and then dried at room temperature. The dried ferrites powders were ground by laboratory-made ball-milling machine and then annealed at 600°Cfor 2 h in vacuum chamber (160 mmHg) by using thermal resistive heating coil. DELTA A Series Temperature Controller DTA4896 and the K-type thermocouple were used as the temperature controller and temperature sensor for the sample preparation. Photograph showing the experimental setup of sample preparation system is shown in Fig 1.

Fig. 1 Photograph of the experimental setup of sample preparation system

UV-VIS-NIR Spectroscopic Measurement

Ultraviolet radiation lies between wavelengths of about 400 nm (1 nm is 10^{-9} m) on the visible-light side and about 10 nm on the X-ray side, though some authorities extend the short-wavelength limit to 4 nm. In physics, ultraviolet radiation is traditionally divided into four regions: near (400–300 nm), middle (300–200 nm), far (200–100 nm), and extreme (below 100 nm).

The (UV-1800) UV-VIS-NIR Spectrophotometer, a product of SHIMADZU Inc., is a solid and robust system fit for these needs. The system is easy to operate and delivers results. The key feature is that it's easy to develop, simple, robust method; this ensures that the methods are followed without mistakes. This is an ideal match for most routine UV-VIS-NIR applications, including regulatory tests, giving fast and reliable results time after time. In the present work, UV-VIS-NIR (Ultraviolet-Visible-Near Infrared) transmission spectra of Nickel substituted Cobalt-Zincferrites with the formula $Co_{0.5-x}Ni_xZn_{0.5}Fe_2O_4$ (where x = 0, 0.1, 0.2, 0.3) were collected on PC-controlled SHIMADZU (UV-1800) UV-VIS-NIR Spectrophotometer in the wavelength range 200 nm – 900 nm. Photograph of the

SHIMADZU (UV-1800) UV-VIS-NIR spectrophotometer is shown in Fig 2. Experimental conditions were used as follows:

        wavelength range :   190 nm – 1100 nm
        bandwidth   :   1 nm (fixed)
        Modes of Operation: scanning, wavelength program, time-drive, rate.

Fig. 2 Photograph of the SHIMADZU (UV-1800) UV-VIS-NIR Spectrophotometer

Results and Discussion

To find the transmission range of the samples, the optical transmission spectra were recorded in the wavelength between 200 and 900 nm was. The collected UV-VIS-NIR transmission spectrum of percentage transmittance "%T" plotted against the wavelength "λ" of $Co_{0.5-x}Ni_xZn_{0.5}Fe_2O_4$ annealed at 600°C are shown in Fig. 3 (a-d). The samples demonstrate that less than 100% transmittance was throughout the Ultraviolet-Visible-Near Infrared region. In the spectrum of x = 0, the intense absorption band was found in the wavelength range about 462 nm – 700 nm. When the increase in dopant concentration of Ni, the intensity and the wavelength of this band was found to be decreased due to the substitution of Ni on Co. In the spectra of x = 0.1-0.3, the transmission of the UV and VIS light increased in the wavelength range from 377 nm – 462 nm and in the wavelength range from 462-900 nm, the transmission of the VIS and NIR light constant or nearly flat band. It can be deduced that the transmission of UV-VIS-NIR light more transparent (wide and stable windows) than the sample of no Ni concentration (x = 0).

The energy band gaps E_g of all the ferrites have been calculated with the help of optical absorption and percentage transmission data. The theory of optical transmission gives the relationship between the absorption coefficient "α" and the photon energy "hν' has a relation; $\alpha = -\ln(1/T)$. From the optical transmission spectrum, the measured transmittance "T" was used to calculate the absorption coefficient "α". To estimate the energy band gap for all the samples, the graph of $(\alpha h\nu)^2$ versus hν has been plotted. The intercept of the line at α= 0 gives the value of energy band gap.

The plots of $(\alpha h\nu)^2$ versus hν of the samples are shown in Fig. 4 (a-d). The values of energy band gaps for all the $Co_{0.5-x}Ni_xZn_{0.5}Fe_2O_4$ (where x = 0, 0.1, 0.2, 0.3) samples annealed at 600°C has been found to be in the range of 3.10eV – 2.85 eV listed in Table 1. Variation of the energy band gap with different concentrations x is shown in Fig. 5. It is observed from Fig 5 that, the energy band gap decreases with increase in concentration of Ni.

The decrease in band gap may be attributed to the variation of structural parameter (lattice constant) with Ni concentration. Sonal Sighal et al. (2011) have reported the energy band gap values of $CrCo_xNi_{1-x}FeO_4$ ferrite in the range 2.30 eV-2.82 eV. Joshi et al. (2003) have prepared nano-composites of $Ni_{1-x}Zn_xFe_2O_4$ with stoichiometric proportion (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) and their energy band gaps values were 1.50 eV - 1.66 eV.
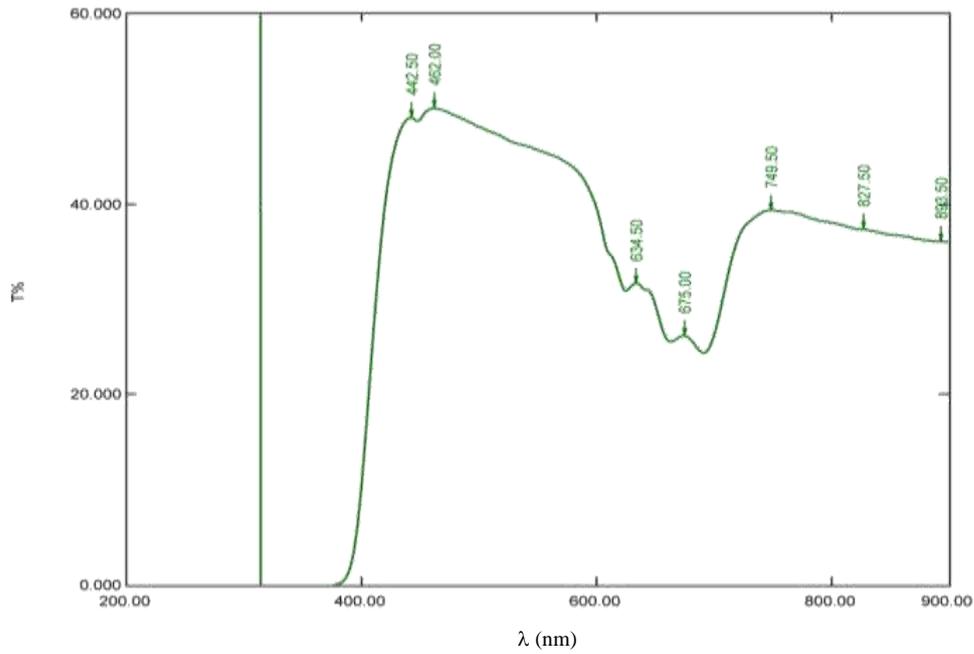

Fig. 3(a) UV-VIS-NIR transmission spectrum of $Co_{0.5-x}Ni_xZn_{0.5}Fe_2O_4(x = 0)$ ferrite
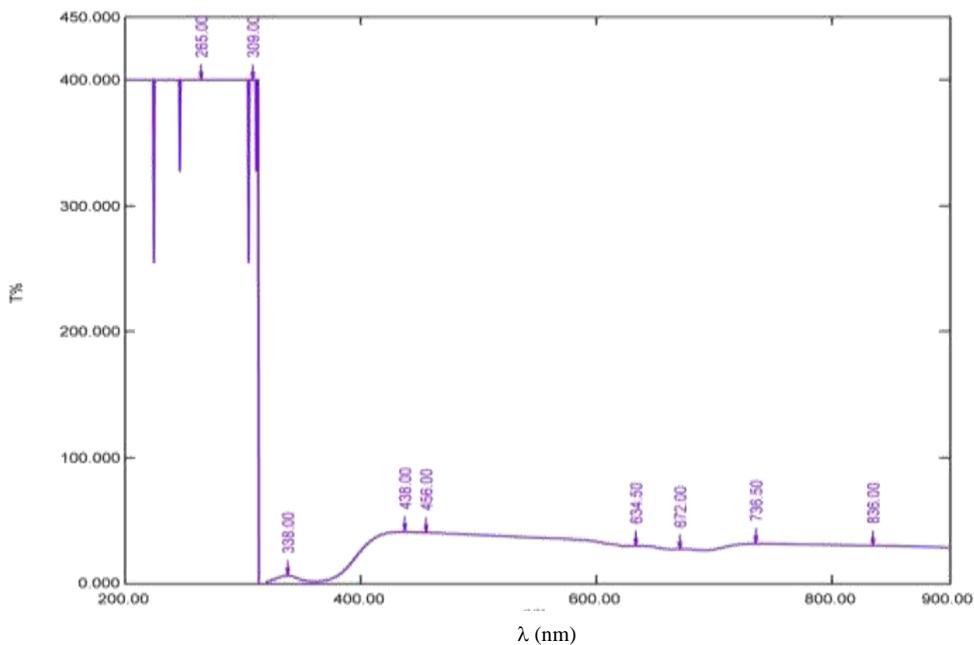
Fig. 3(b) UV-VIS-NIR transmission spectrum of $Co_{0.5-x}Ni_xZn_{0.5}Fe_2O_4(x = 0.1)$ ferrite
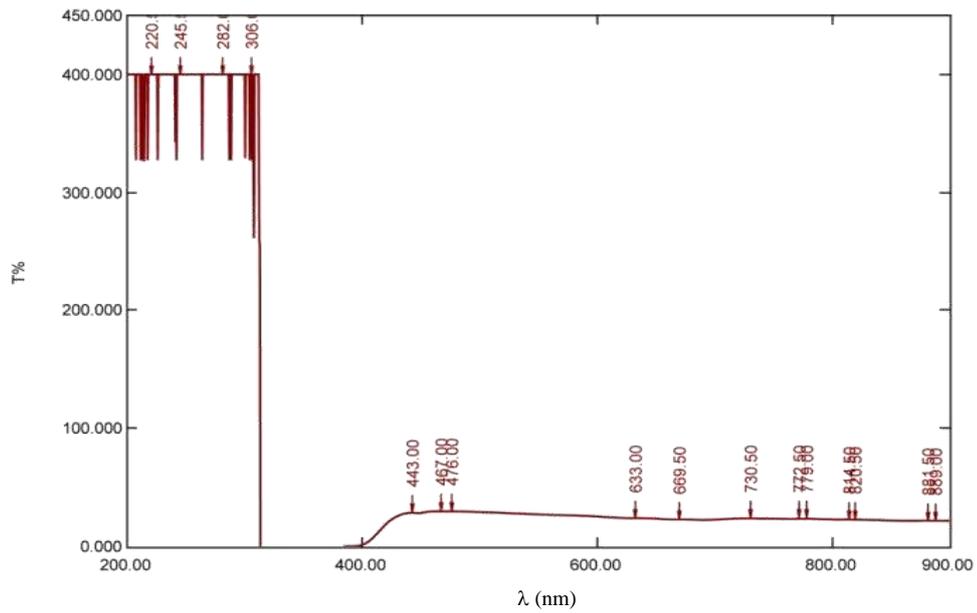
Fig. 3(c) UV-VIS-NIR transmission spectrum of $Co_{0.5-x}Ni_xZn_{0.5}Fe_2O_4$ (x = 0.2) ferrite
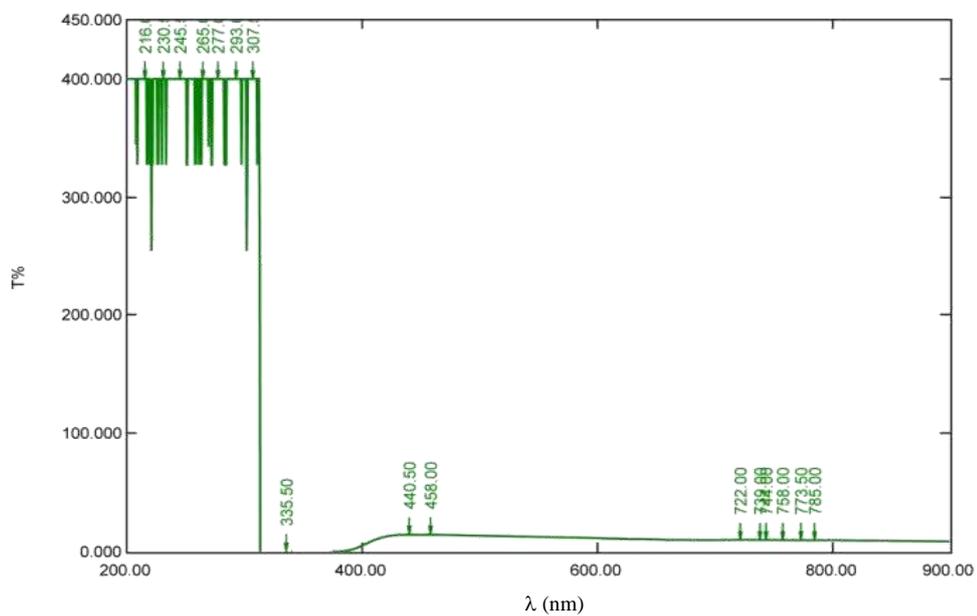
Fig. 3(d) UV-VIS-NIR transmission spectrum of $Co_{0.5-x}Ni_xZn_{0.5}Fe_2O_4$ (x = 0.3) ferrite
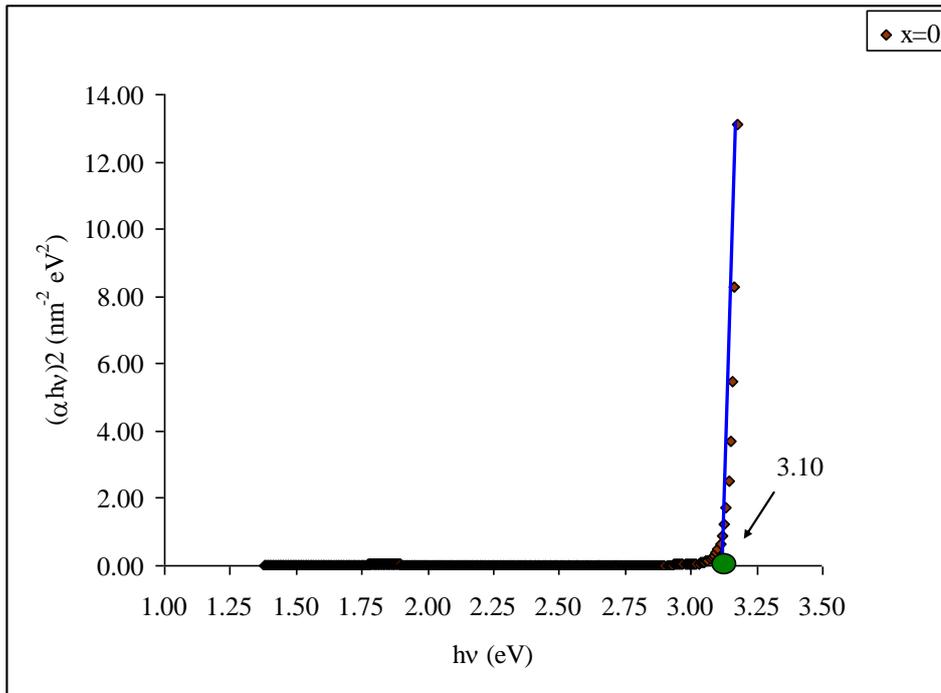
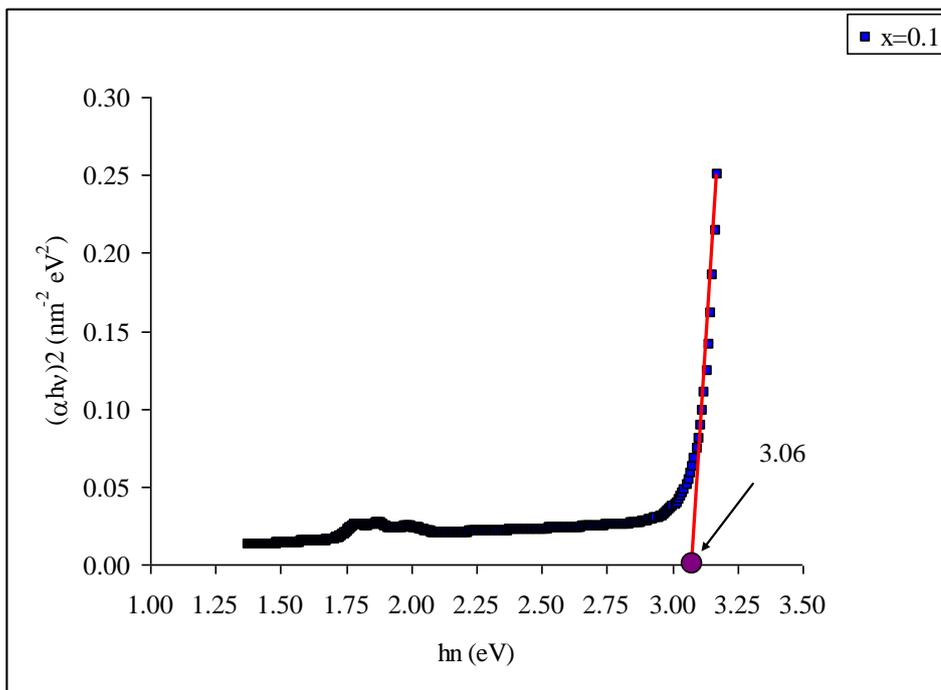Fig. 4(a) Plot of $(\alpha h\nu)^2$ versus $h\nu$ of the $Co_{0.5-x}Ni_xZn_{0.5}Fe_2O_4$ (x = 0) ferrite

Fig. 4(b) Plot of $(\alpha h\nu)^2$ versus $h\nu$ of the $Co_{0.5-x}Ni_xZn_{0.5}Fe_2O_4$ (x = 0.1) ferrite
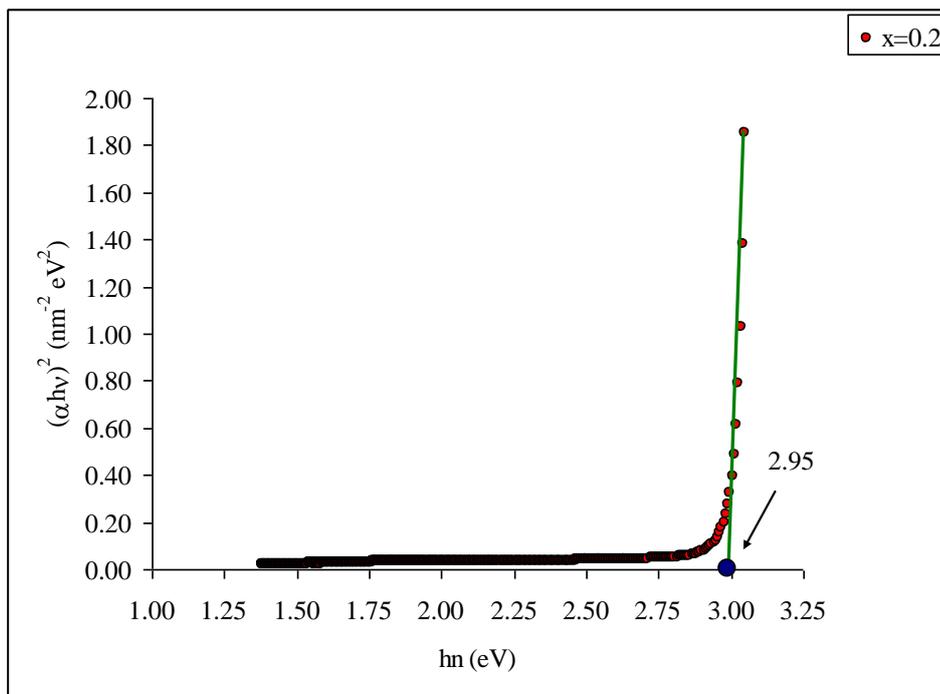
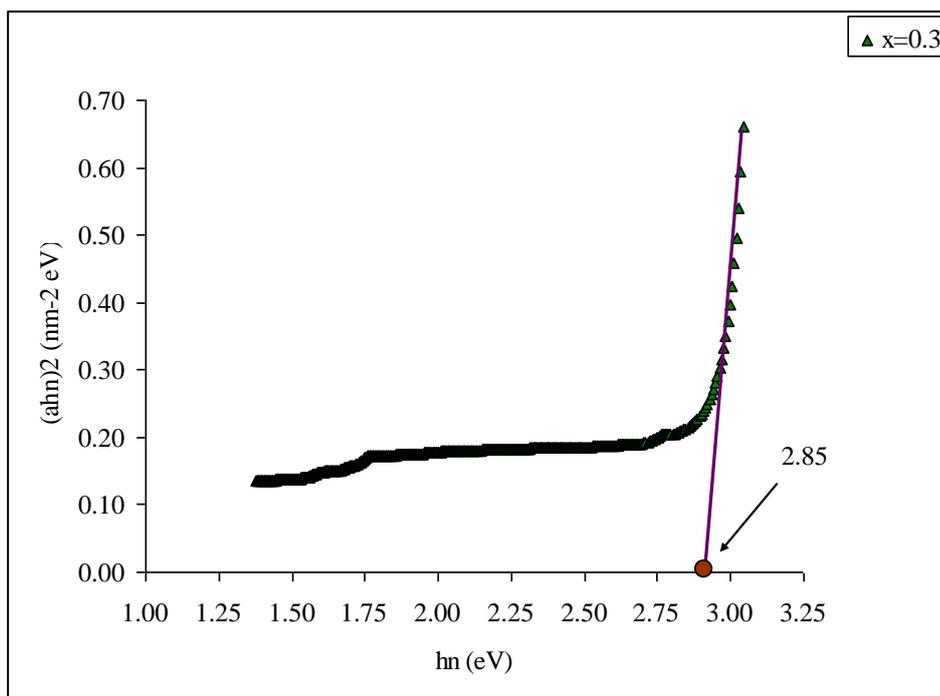Fig. 4(c) Plot of $(\alpha h\nu)^2$ versus $h\nu$ of the $Co_{0.5-x}Ni_xZn_{0.5}Fe_2O_4$ (x = 0.2) ferrite

Fig. 4(d) Plot of $(\alpha h\nu)^2$ versus $h\nu$ of the $Co_{0.5-x}Ni_xZn_{0.5}Fe_2O_4$ (x = 0.2) ferrite

Table 1 Energy band gaps of $Co_{0.5-x}Ni_xZn_{0.5}Fe_2O_4$ ferrites

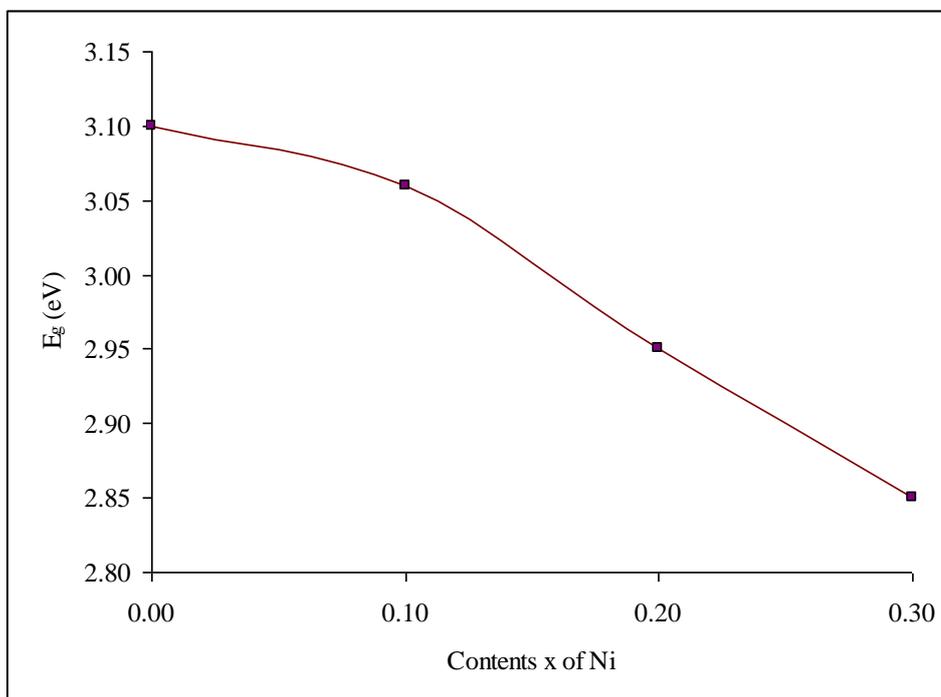| Sr. No.	Contents x of Ni	E_g (eV)
1	0	3.10
2	0.1	3.06
3	0.2	2.95
4	0.3	2.85

Fig. 5 Variation of the energy band gap with different Ni concentration in $Co_{0.5-x}Ni_xZn_{0.5}Fe_2O_4$ ferrites

Conclusion

Nickel substituted Cobalt-Zinc ferrites with the formula $Co_{0.5-x}Ni_xZn_{0.5}Fe_2O_4$ (where x= 0, 0.1, 0.2, 0.3) were successfully prepared by co-precipitation method. In the collected UV-VIS-NIR absorption spectra, the cut off wavelength about 435 nm along with a large transmission window in the entire visible and near infrared region is found. Also the optical transmittance range is throughout the entire visible and infrared region (i.e., 390 nm – 1100 nm). The experimentally observed band gap increase with the increase in the concentration of Ni suggests that the variation of structural parameter (lattice constant) occurring in the sample is responsible for such a variation.

Acknowledgements

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