

A Low Temperature Synthesis and Optical Characterization of Mn-Ni Mixed Nanoferrites

Elangbam Chitra Devi* and Ibetombi Soibam

Department of Physics, National Institute of Technology Manipur, Langol – 795004, Manipur, India;
elangbam_chitra@rediffmail.com, ibetombi96@gmail.com

Abstract

Objectives: The presented work investigates the optical properties of Mn-Ni mixed nanoferrites prepared by a low temperature synthesis method. **Methods:** A series of manganese nickel (Mn-Ni) mixed spinel nanoferrites having chemical formula $Mn_{1-x}Ni_xFe_2O_4$ ($x=0.1, 0.2, 0.3, 0.4, 0.5$) have been synthesized by a simple chemical co-precipitation method. The spinel phase formation of the prepared nanoferrites was confirmed using x-ray diffraction (XRD). Optical properties were investigated using UV-visible absorption spectroscopy recorded in the range 200 to 900 nm. Using the absorption spectra and Tauc's relation, the band gap was estimated. **Findings:** The prepared nanoferrites possess narrow band gap. It was observed that concentration of nickel has profound effect on the optical band gap. A remarkable decrease in the optical band gap was observed with increasing nickel concentration revealing the tunability of the optical band gap by compositional variation of the nanoferrites. **Application:** The prepared magnetic nanoparticles owing to its large surface to volume ratio with tunable narrow band gap may find applications in photocatalysis, dye degradation, waste water treatment technology etc.

Keywords: Low Temperature Synthesis, Nanoparticles, Optical Band Gap, Spinel Ferrites

1. Introduction

There have been enormous studies on ferrites as potential candidate in the vast electronic industries because of its desirable magnetic and electrical properties¹⁻³. They were found to be used as recording and memory devices, transformers, antenna rods, microwave devices, gas sensors etc^{1,2}. Apart from the electronic industries, they were also found to be used in biotechnological applications such as drug delivery agents, hyperthermia applications, medical diagnosis etc^{4,5}. Recently, there has been an aroused interest in the study of ferrites as photocatalyst for removal of toxic pollutants such as Cr (VI) by the process of photocatalytic reduction^{6,7}. An investigation on the optical properties of ferrites is of great importance from the practical point of view as knowledge of the optical properties of these materials helps in incorporating them in the field of optical devices, photocatalytic applications etc. The optical band gaps were reported to be dependent on the composition and size of

the materials^{8,9}. Thus either by changing the composition or size, the band gap of the materials can be designed for specific application. So, in the present work nickel has been incorporated in manganese ferrite ($MnFe_2O_4$) system to observe the compositional variation of the band gap. Co-precipitation method is an effective route for the synthesis of nanoparticles with uniform composition and short reaction time giving high yield. Hence it was adopted for synthesis of the nanoparticles. The presented method does not require any further heat treatment. So, the ferrite nanoparticles were simply obtained through a low temperature chemical synthesis method.

2. Experimental Details

2.1 Materials

For the synthesis of Mn-Ni mixed ferrite nanoparticles, stoichiometric amounts of manganese (II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$, purity ~ 99%) from Merck, Mumbai, Iron (III) chloride anhydrous ($FeCl_3$, purity

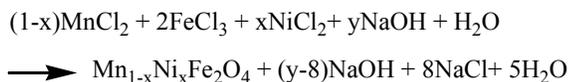
* Author for correspondence

~ 98%) from Merck, Mumbai and Nickel (II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, purity ~ 99%) from Merck, Mumbai were used as starting materials and sodium hydroxide (NaOH , purity ~ 97%) from Merck, Mumbai was used as precipitating agent. The deionized water from Merck, Mumbai was used as solvent.

2.2 Sample Preparation

Nickel doped manganese ferrite nanoparticles were prepared by co-precipitation method. The starting materials were Manganese (II) Chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$), Iron (III) Chloride anhydrous (FeCl_3), Nickel (II) Chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) and Sodium Hydroxide (NaOH). For a typical synthesis of $\text{Mn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$, aqueous solution of 0.5 M MnCl_2 , 0.5 M NiCl_2 and 1M FeCl_3 was mixed at 80°C with continuous stirring. It was then added to 0.64M boiling NaOH solution with continuous stirring. The solution was maintained at 95°C for 1 hour and the precipitate obtained was centrifuged. It was washed several times with distilled water and dried at 70°C after which the products were grounded into fine powders. The powder so obtained was subjected to characterization.

The chemical reaction may be expressed as:



2.3 Characterization

Phase structure of all the prepared samples was characterized by X-ray diffraction (XRD) with Cu-K_α radiation. The absorption spectra were recorded using a Perkin Elmer UV-visible spectrometer. All the measurement was performed at room temperature.

3. Results and Discussion

3.1 XRD Analysis

The spinel phase formation of the prepared samples was confirmed by x-ray diffraction studies and is shown in Figure 1. It reveals pure spinel phase of ferrites. The observed diffraction peaks are indexed by the spinel structure of MnFe_2O_4 with JCPDS card number 74-2403. Average crystallite size were calculated using Debye Scherrer formula,

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

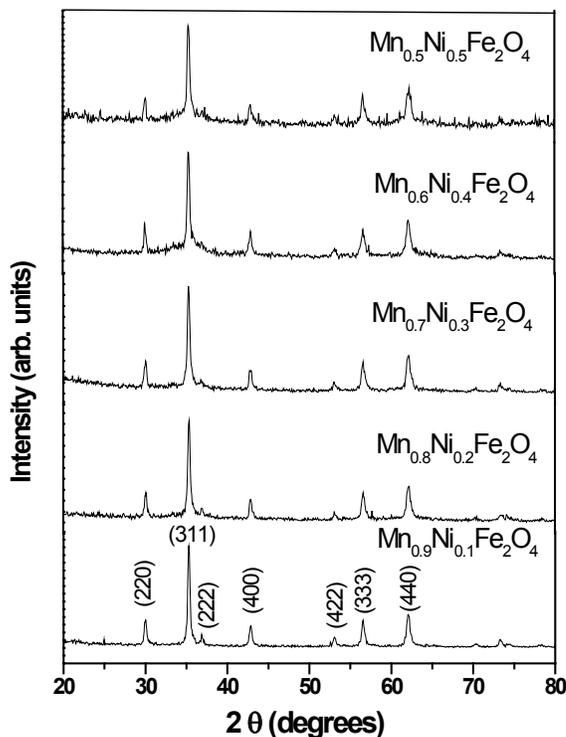


Figure 1. XRD pattern for Mn-Ni mixed nanoferrites.

and are graphically presented in Figure 2. It was observed that the average crystallite sizes were found to be in the range 21.16 to 26.38 nm depending on the nickel concentration. A detail explanation on the effect of nickel doping on the crystallite size, lattice constant etc have been reported elsewhere¹⁰.

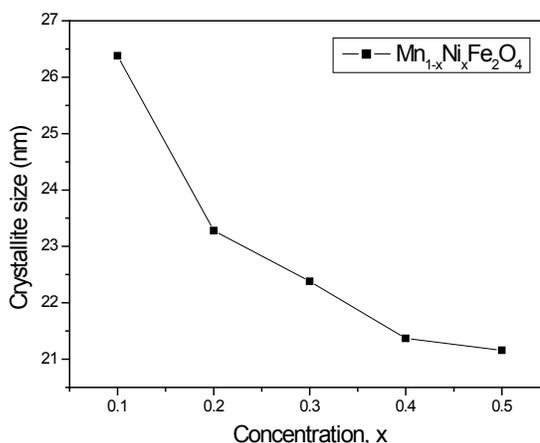


Figure 2. Variation of crystallite size with varying nickel concentration.

3.2 UV-Visible Spectroscopy

The UV-Visible absorption spectroscopy is one of the

important techniques for the investigation of the optical properties of materials. The colloidal solutions of ferrite nanoparticles prepared by sonication in double distilled water were used for recording the spectra. The absorption spectra of the prepared samples recorded in the range 200-900 nm is shown in Figure 3.

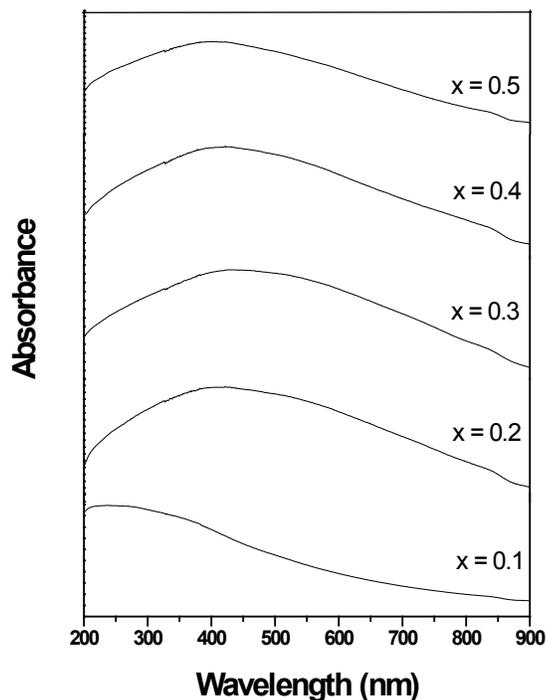


Figure 3. Absorption spectra for $Mn_{1-x}Ni_xFe_2O_4$ ($x = 0.1, 0.2, 0.3, 0.4, 0.5$) nanoparticles.

It can be seen from the absorption spectra that the absorption hump in the ultra violet region around 300 nm (in case of $Mn_{0.9}Ni_{0.1}Fe_2O_4$) shifts toward longer wavelength visible region with the increase in nickel concentration. To study the effect of nickel concentration on the optical band gap the absorption data were fitted into Tauc equation⁸

$$(\alpha hv)^n = C(hv - E_g) \tag{2}$$

where C is proportionality constant, h is Planck constant, E_g is band gap, n is either 2 for direct band gap or $\frac{1}{2}$ for indirect band gap transition and α is the absorption coefficient determined from the absorption data, using the relation:

$$\alpha = 2.303 \left(\frac{A}{t} \right) \tag{3}$$

where A is the absorption and t is the thickness of the sample (i.e., thickness of the cubet and is equal to 10 mm).

Tauc plot in which $(\alpha hv)^n$ was plotted as a function of photon energy hv for all the nickel concentration are shown in Figure 4-8. The best linear fitting is observed for $n = 2$ which reflects a direct band gap nature of the prepared samples. By extrapolating the straight portion of the curve to the energy axis in the graph, the band gap of the nanoferrites was estimated. The band gap of the samples was found to vary from 1.2 eV - 2.5 eV with the variation in nickel concentration (graphically presented in Figure 9). Thus, the estimated value of band gap decreases with the increase in nickel concentration. This may have arisen due to the additional sub-band-gap energy levels induced due to the introduction of the nickel^{8,9}. Hence, by introducing nickel in manganese ferrite the absorption spectra and hence the band gap can be tuned. The concentration of the nickel can be used to engineer the band gap for specific applications.

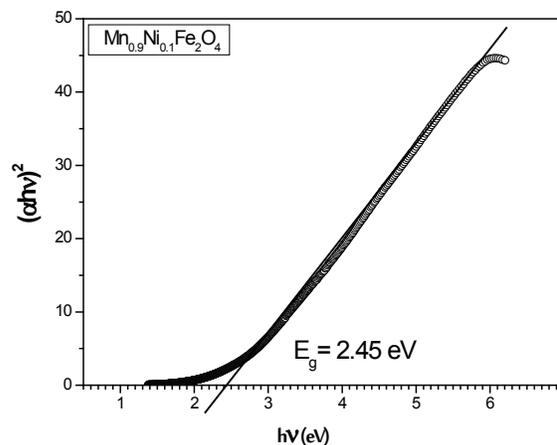


Figure 4. Tauc plot for $Mn_{0.9}Ni_{0.1}Fe_2O_4$ nanoparticles.

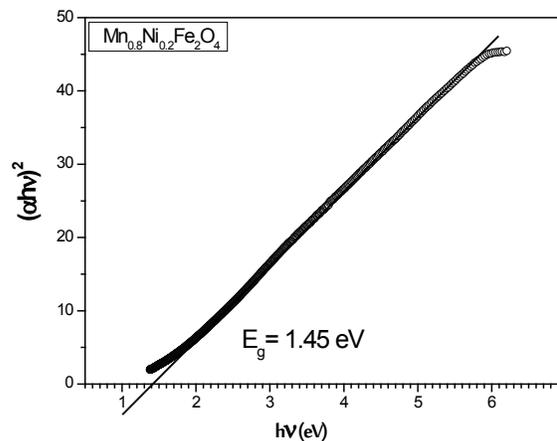


Figure 5. Tauc plot for $Mn_{0.8}Ni_{0.2}Fe_2O_4$ nanoparticles.

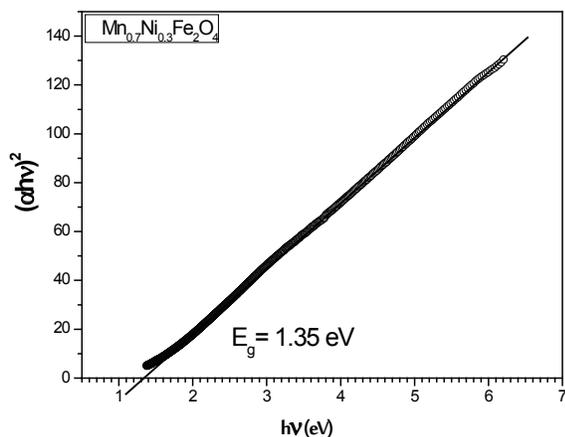


Figure 6. Tauc plot for Mn_{0.7}Ni_{0.3}Fe₂O₄ nanoparticles.

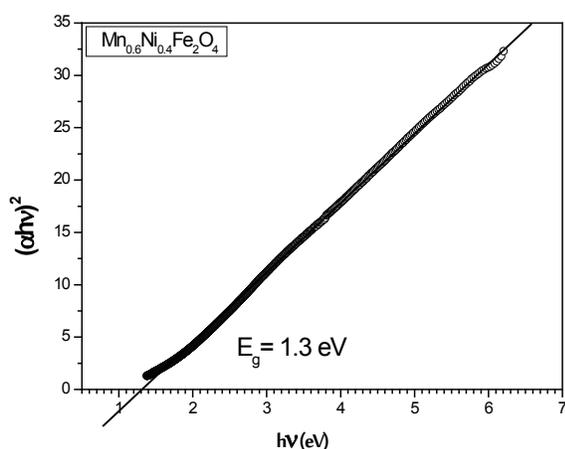


Figure 7. Tauc plot for Mn_{0.6}Ni_{0.4}Fe₂O₄ nanoparticles.

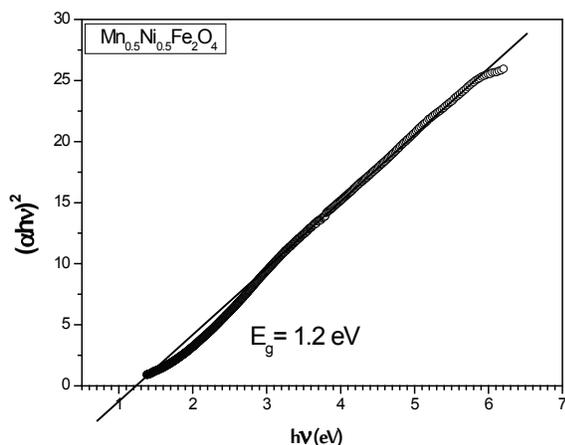


Figure 8. Tauc plot for Mn_{0.5}Ni_{0.5}Fe₂O₄ nanoparticles.

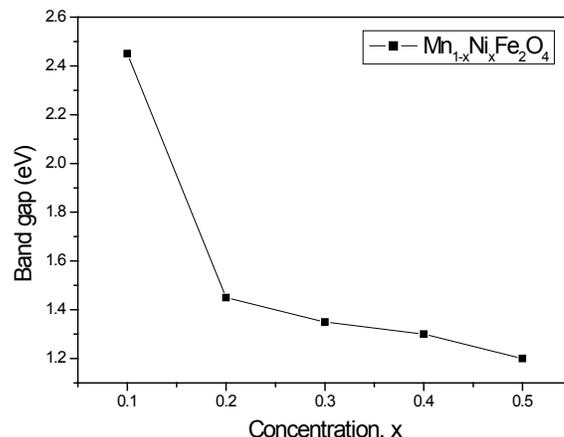


Figure 9. Variation of band gap with nickel concentration.

4. Conclusion

A facile low temperature chemical co-precipitation method without any further heat treatment was adopted for the synthesis of Mn-Ni mixed nanoferrites. XRD reveals the pure spinel structure of ferrite. The average crystallite size, calculated from XRD data was found to be in the range 21.16 nm - 26.38 nm. The effect of nickel concentration on the optical properties of the nanoparticles was studied and it was observed that the absorption spectra as well as the band gap were found to be strongly dependent on nickel concentration. The optical band gap was found to decrease from 2.45 eV to 1.2 eV with the increase in nickel concentration. Thus, it can be concluded that by changing nickel concentration, the optical properties of Mn-Ni mixed ferrite nanoparticles can be tuned and hence may be optimized for applications in various fields of science and technology such as solar cell technologies, opto-electronic devices, photovoltaic and photocatalytic applications.

5. Acknowledgements

The authors wish to thank Department of Physics, Manipur University for XRD measurement and Dr. Th. David Singh (Department of Chemistry) of NIT Manipur for UV-visible spectroscopy measurement.

6. References

1. Manikandan A, Vijaya JJ, Kennedy LJ, Bououdina M. Structural optical and magnetic properties of $Zn_{1-x}Cu_xFe_2O_4$ nanoparticles prepared by microwave combustion method. *Journal of Molecular Structure*. 2013 Mar; 1035:332-40. Crossref
2. Gopalan EV, Malini KA, Sagar S, Kumar DS, Yoshida Y, Al-Omari IA, Anantharaman MR. Mechanism of ac conduction in nanostructured manganese zinc mixed ferrite. *Journal of Physics D: Applied Physics*. 2009 Jul; 42(16). Crossref
3. Devi EC, Soibam I. Effect of Zn doping on the structural, electrical and magnetic properties of $MnFe_2O_4$ nanoparticles. *Indian Journal of Physics*. 2017 Mar; p. 1-7. Crossref
4. Doaga A, Cojocariu AM, Amin W, Heib F, Bender P, Hempelmann R, Caltun OF. Synthesis and characterizations of manganese ferrites for hyperthermia applications. *Materials Chemistry and Physics*. 2013 Dec; 143(1):305-10. Crossref
5. Sahoo B, Devi K SP, Dutta S, Maiti TK, Pramani KP, Dhara D. Biocompatible mesoporous silica coated superparamagnetic manganese ferrite nanoparticles for targeted drug delivery and MR imaging applications. *Journal of Colloid and Interface Science*. 2014 Oct; 431:31-41. Crossref PMID:24980623
6. Ali IO, Mostafa AG. Photocatalytic reduction of chromate oxyanions on $MMnFe_2O_4$ (M=Zn, Cd) nanoparticles. *Material Science in Semiconductor Processing*. 2015 May; 33:189-98. Crossref
7. Zhao X, Wang W, Zhang Y, Wu S, Li F, Liu JP. Synthesis and characterization of gadolinium doped cobalt ferrite nanoparticles with enhanced adsorption capability for Congo red. *Chemical Engineering Journal*. 2014 Aug; 250:164-74. Crossref
8. Gosh PK, Ahmed SF, Jana S, Chattopadhyay KK. Photoluminescence and field emission properties of ZnS:Mn nanoparticles synthesized by rf-magnetron sputtering technique. *Optical Materials*. 2007; 29(12):1584-90. Crossref
9. Manikandan A, Vijaya JJ, Sundarajan M, Meganathan C, Kennedy LJ, Bououdina M. Optical and magnetic properties of Mg-doped $ZnFe_2O_4$ nanoparticles prepared by rapid microwave combustion method. *Superlattices and Microstructures*. 2013 Dec; 64:118-31. Crossref
10. Devi EC, Soibam I. Structural and electrical studies of Mn-Ni mixed nanoferrites (In press). *International Journal of Nanoparticles*.