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Phase Evolution & Characterization of Spinel Ferrite (Oxide) Nanocomposite material Prepared by Chemical Route

Soumya Mukherjee, Abhigyan Datta, Mrinal Saha, Siddhartha Mukherjee[1]
[1] Department of Metallurgical & Material Engineering, Jadavpur University, Kolkata-700032, India
Corresponding E-mail: sm_n4@yahoo.co.in, smmukherjee3@gmail.com

Abstract

Nanocomposite of Nickel Ferrite-Zinc Ferrite (Spinel Oxide ferrites) was prepared by co-precipitation route from metal nitrate precursors using 1:1 molar ratio. DSC-TGA of the mixed powder was studied to observe thermal behaviour and crystallization temperature for proper phase development. Heat treatment was carried out at 700^0, 750^0 C for 3, 4 and 5hrs for synthesizing the nanocomposite. XRD analysis was done to determine the phases, plane of orientation of respective phases of the nanocomposite while crystallite size was measured by Scherrer's formula. Highly pure samples with proper orientation of phases developed for the nanocomposite was obtained at 700^0, 750^0C for 5hours soaking period. SEM (Scanning electron Microscope) was taken to obtain the morphology and structural analysis. Interconnected agglomerates with spherical and polygonal shape particulate morphology was obtained in the nanocomposite material. The materials were characterized by FTIR to determine the stretching and vibration of bonds with proper co-ordination required followed by UV-VIS spectral analysis. Bandgap was evaluated from the spectra using Tauc relation.

Keywords: *Nickel Ferrite-Zinc Ferrite, Nanocomposite, XRD, FTIR, HRSEM, UV-VIS.*

1. Introduction

Nanocrystalline spinel ferrites have been the subject of interest due to their enhanced optical, magnetic, and electrical properties, in compare to bulk counterparts. Nanospinel ferrites have variety of applications, like electrodes in energy storage devices, catalysts, and magnetic storage devices. Among various ferrites, which form a major constituent of the magnetic ceramic materials, nanosized nickel ferrite possesses attractive properties for the application as soft magnets, core materials in power transformers and low loss materials at high frequencies. High permeability in the radio frequency region, high electrical resistivity, high Curie temperature and low eddy current loss are important properties of nickel ferrites, which make them suitable for wide range of applications. Nickel ferrite has inverse spinel structure. The crystal structure is face centred cubic with the unit cell containing 32 O^{2-}, 8 Ni^{2+} and 16 Fe^{3+} ions. The oxygen ions form 64 tetrahedral and 32 octahedral sites, where 24 cations are distributed. The eight Ni^{2+} and eight Fe^{3+}cations occupy half of the octahedral sites and the other eight Fe^{3+} ions occupy eight tetrahedral sites. Ferrimagnetic property of the material arises from magnetic moments of anti-parallel spins between Fe^{3+} ions at tetrahedral sites and Ni^{2+} and Fe^{3+} ions at octahedral sites. $ZnFe_2O_4$ is a promising semiconductor photo-catalyst for various processes, due to its ability to absorb visible light and its high efficiency shows potentially wide applications in photoinduced transformer, photoelectrochemical cells and photochemical hydrogen production. It is known that bulk zinc ferrite represented by the chemical composition $ZnFe_2O_4$ crystallizes in the normal spinel structure with Zn^{2+} ions in the tetrahedral A-sites and Fe^{3+} ions in the octahedral B-sites and it is antiferromagnetic with a Neel temperature of about 10K due to the B–B interactions, and above that temperature, they are paramagnetic. It is therefore likely that in nanocrystalline zinc ferrite due to strain, the cation distribution changed from normal to mixed spinel type. Thus, a small number of Fe^{3+}ions occupy the tetrahedral A-sites and these ions switch on the A–B super-exchange interaction, leading to a larger magnetization. In other words, the magnetic ordering introduced in nanocrystalline zinc ferrites occurs because of strong A–B interaction between Fe^{3+} ions in the octahedral B-sites and Fe^{3+} ions in the tetrahedral A-sites, which are forced into these respective positions during the synthesis of nanoparticles. Synthesis and magnetic studies on Ni-ferrite and Zn-ferrite as well as Ni-Zn ferrite has been carried out for over a decade. $Ni0.5Zn0.5Fe_2O_4$ nano-particles were synthesized via sol-gel route in a silica matrix followed by calcinations at 700-900^0C. The absence of saturation magnetization at 10 kOe and Mossbauer spectra confirm super-paramagnetism of Ni-Zn Ferrite.[1] Effect of preparation method on structure and properties of Nickel ferrite were studied by producing $Ni0.8Zn0.2Fe_2O_4$ via the conventional

ceramic route (oxide precursors) and also through co-precipitation route (metal nitrate precursors and ammonium hydroxide precipitation).[2] Nanosized Ni-Zn ferrites were also prepared using reverse micelle route using AOT/iso-octane at room temperature without requiring any subsequent firing of the material.[3]
However, not much work has been reported on preparation of composites of Ni-ferrite and Zn-ferrite nano-particles instead of Ni-Zn intermetallic ferrite. In this endeavor we have synthesized Ni ferrite- Zn ferrite nanocomposite via coprecipitation method. Coprecipitation method was used due to its distinct advantages such as high production rate, small particle size, lower temperatures than conventional ceramic route and low cost of starting material (TEOS used in sol-gel is costly). Since composite exhibits properties as volume fraction of the constituent phases, we can get the advantages of Ni-ferrite as a super-paramagnetic material and Zn-ferrite as a photocatalyst, chemical sensor in the same composite. Nanocomposite synthesized was characterized by XRD for phase identification, morphology by SEM along with structural information, bandgap evaluation using Tauc relation from UV-VIS spectra and FTIR spectra determining the bond co-ordination of the nanocomposite.

2. Experimental procedure

Chemical coprecipitation route was performed to synthesize nanocomposite of Nickel Ferrite-Zinc Ferrite. AR grade Nickel nitrate, Ferric Nitrate, Zinc Nitrate and Ammonium Hydroxide (Merck India) was used as precursors for synthesizing the nanocomposite material. At first hydroxides of Ni, Fe and Zn, Fe were obtained by dissolving the respective nitrate salts in 1:2 molar ratio in double distilled water with constant stirring at about 70-80°C, followed by addition of ammonium hydroxide to obtain the precipitate of respective (Ni,Fe & Zn,Fe) hydroxides. Hydroxides obtained were filtered and dried at 80°C for certain period till all hygroscopic matters were eliminated. The dried respective hydroxide powders were then mixed properly in agate mortar in 1:1 molar ratio. A part of powder was put in DSC-TGA analyzer (Perkin Elmer, Pyris Diamond 480) for thermal analysis and to observe the zone of crystallization. Mixed powders were then put in furnace for heat treatment in air atmosphere at temperatures of 700°C, 750°C for 3, 4 and 5hrs respectively. Phases were determined from the developed powder crytallites by means of X-ray Diffraction (Rigaku, Ultima III Cu K_α of 1.54Å source). The crystallite size was calculated using Scherrer's formula $t=0.9\lambda/\beta\cos\theta$ and plane of orientation was also identified. Morphology was observed by means of HRSEM (Jeol, JSM-6360 Scanning Electron Microscope). FTIR analysis (IR Prestige-21, Shimadzu) was done to observe the vibration and stretching of the required bond formed in the nanocomposite. UV-VIS spectroscopy (Perkin Elmer, Lamda 35) was performed to evaluate the bandgap of the nanocomposite.

3. Results & Discussions

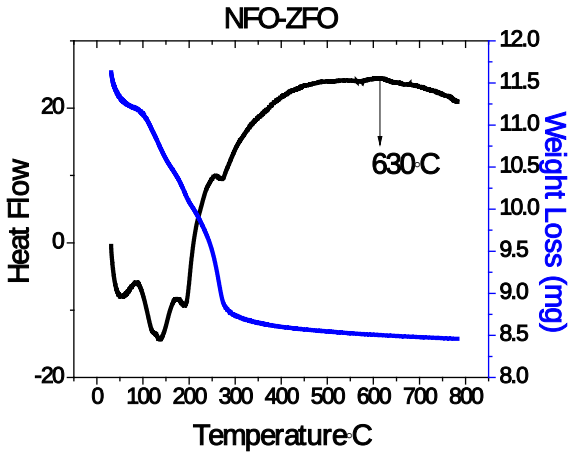


Fig1. DSC-TGA plot of NFO-ZFO for nanocomposite formation

From thermal analysis plot of DSC-TGA (Fig1), it was observed that upto 300°C there was drastic weight loss accompanied with one prominent endothermic trough at about 130°C. After 300°C, weight loss was found to be negligible followed by a broad exothermic hump. Weight loss may be due to loss of water of crystallization and residual ammonium hydroxide used for precipitation to synthesize the nanocomposite. The broad exothermic hump was found to initiate at about 450°C. Broad exothermic peak corresponds to crystallization zone/sintering range for phase development of the required nanocomposite material. Ferrite was found to form at about 630°C. From this thermal analysis, heat treatment schedule was selected to develop the spinel ferrite nanocomposite.

Heat treatment was carried out in air at 700°C, 750°c for 3, 4 and 5 hours for the synthesis of nanocomposite material.

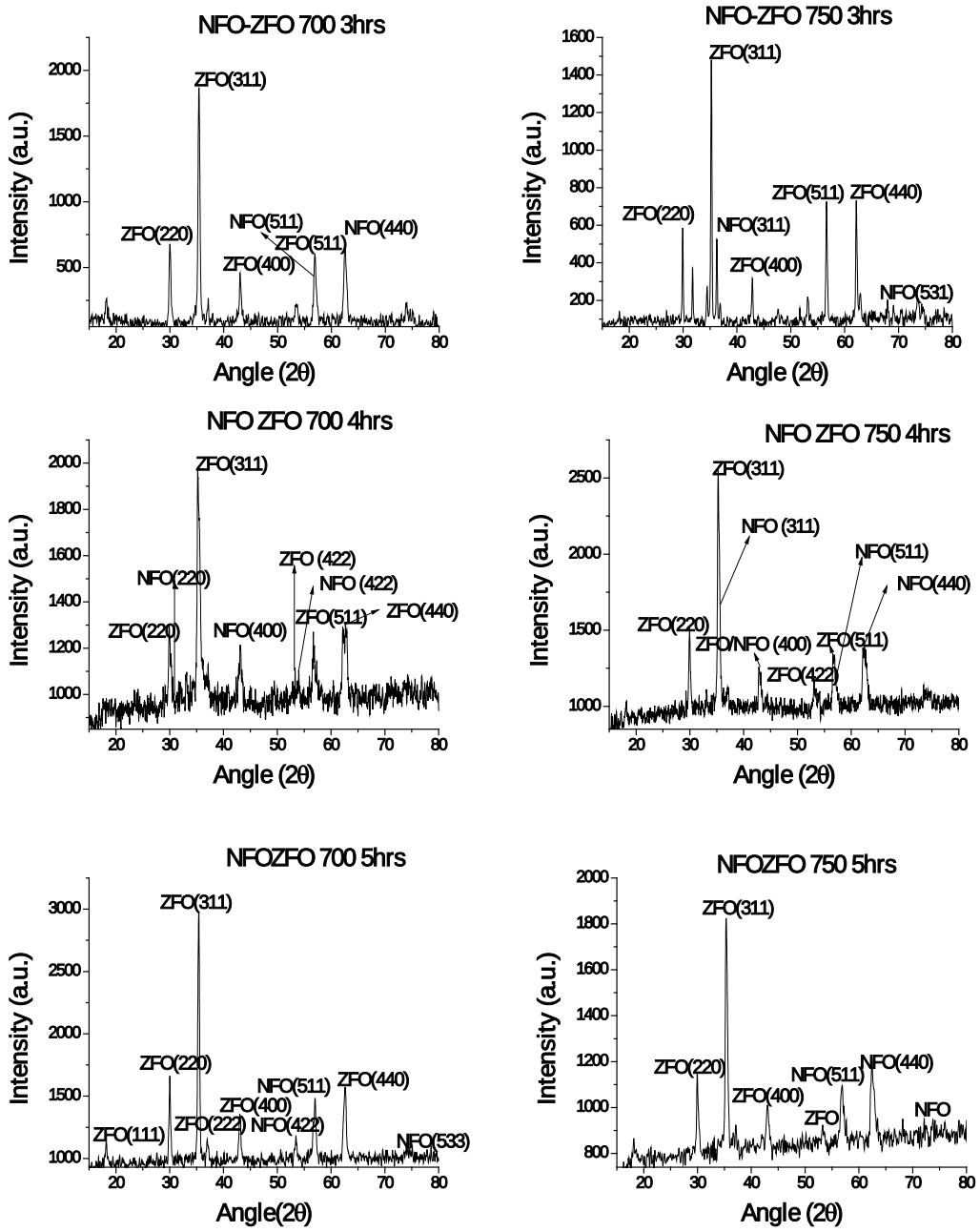


Fig 2. XRD plots of NFO ZFO nanocomposite after heat treatment at 700 and 750 for 3, 4 and 5 hours

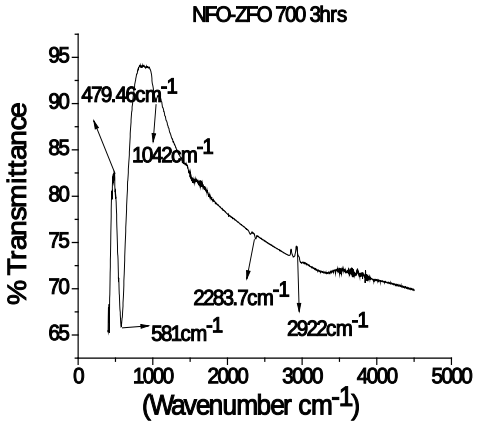
The phases developed after heat treatment within the nanocomposite was determined by using XRD (X-ray Diffraction) with Cu Kα source of 1.54A° wavelength (Fig-2). In all the cases, Zinc ferrite (ZFO) spinel was formed within the nanocomposite with highest peak along (311) plane. Crystallite size was measured using Scherrer's formula $t=0.9\lambda/\beta\cos\theta$ for ZFO phase. Crystallite size of ZFO was found to be maximum at 750^0C, 3hrs (among 750 series) and at 700^0C, 4 hrs (among 700 series) having values 44.32nm & 70.6nm respectively. Other prominent peaks of Zinc ferrite were found to be oriented along (220), (400), (511) plane. Inverse-spinel Nickel ferrite was found to be prominent along (311), (440), (220) and (511) plane. Both inverse-normal spinel ferrites with their high intense peak along (311) plane was obtained after heat treatment at 750°C for 3 and 4 hours respectively. Highest crystallite size for nickel ferrite was found to be 70.7nm at 750°C at 4hours soaking period. At 700°C, for 4 hours soaking period treatment leads to formation of both ferrites having closest

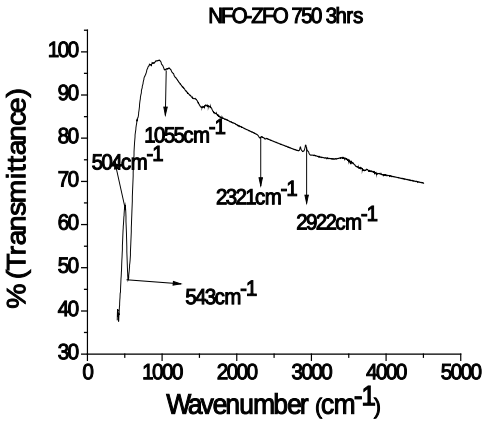
crystallite size. A comparative study of nanocomposite samples treated at different temperature, time and evaluation of crystallite size was shown below in Table1.

Table1. Nanocomposite synthesized at different temperatures, soaking period with variation in crystallite size

Sample Name	Heat treatment temperature	Soaking time	Crystallite size (nm) & Planes of orientation
NFOZFO	700	3	29.6 nm for ZFO (311) plane & 65.85 nm for NFO (440) plane
NFOZFO	750	3	44.32 nm for ZFO (311) plane & 55.96 nm for NFO (311) plane
NFOZFO	700	4	70.6 nm for ZFO (311) plane & 69.7 nm for NFO (220) plane
NFOZFO	750	4	35.5 nm for ZFO (311) plane & 70.7 nm for NFO (311) plane
NFOZFO	700	5	23.61 nm for ZFO (311) plane & 23.23 nm for NFO (440) plane
NFOZFO	750	5	20.13nm for ZFO (311) plane & 49.39nm for NFO (440) plane

From the Table-1, it was observed that there were no certain trends for better crystallite growth with the effect of temperature and time of individual ferrites formation.





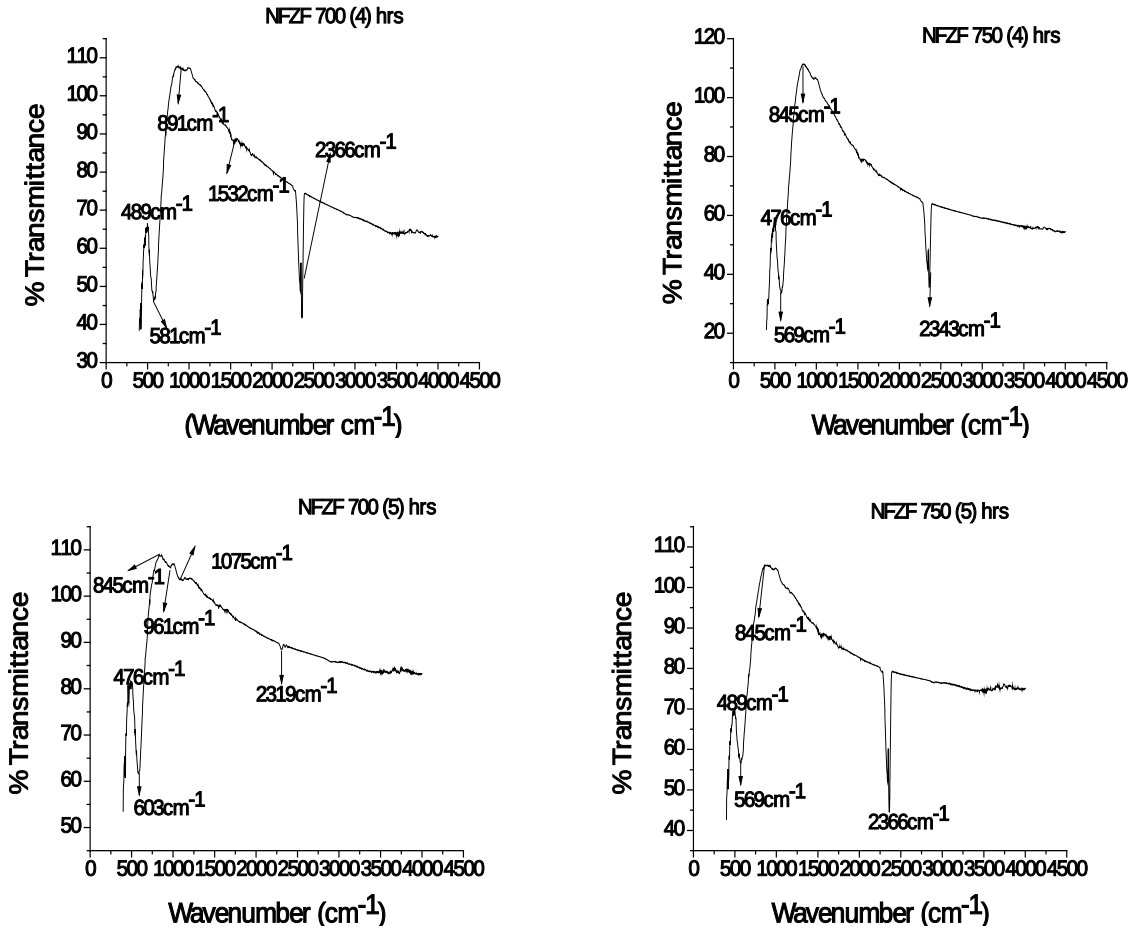


Fig 3 . FTIR spectra plots of NFO ZFO after heat treatment at 700 and 750 for 3, 4 and 5 hours

From FTIR spectra (Fig-3) in transmittance mode, stretching and vibration of bonds for the nanocomposite was observed. Here the mid IR spectra of the samples synthesized at 700°C, 750°C for 4, 5 hours were noted. Frequency bands were found to be sensitive to the co-ordination of cation-anion in octahedral and tetrahedral positions, which were found in the range of 600-540 and 450-400cm^{-1} [4], [5]. In our experiment, absorption bands were observed at about 480cm^{-1} and 569-603cm^{-1}, thus confirming with the results of the previous workers. Hence, proper phase development from XRD study coupled with stretching and vibration of the required bonds as per the co-ordination of cations in octahedral and tetrahedral positions confirm the successful synthesis of nanocomposite of ferrite spinel system.

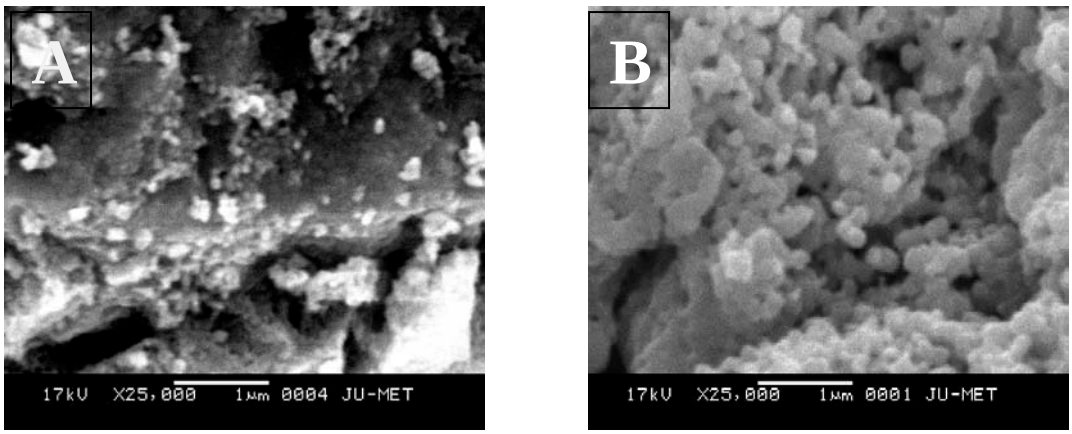


Fig4. Morphology from SEM at 25000X for the nanocomposite of NFO-ZFO synthesized at 700^{0}C, 5 hrs and at 750^{0}C, for 3hrs

Fig-4 shows the Morphology of the prepared nanocomposite studied using SEM (Scanning Electron Microscope) at magnification of 25,000 with 1μ resolution . Powdered samples were coated with Pd in Jeol (JFC-1600 Autofine spin coater) to make it conducting to generate the image properly by backscattered electrons. Interconnected agglomerates were obtained for the prepared nanocomposite sample. Agglomerates were also found to have spherical shape and irregular slightly elongated particulates being dispersed throughout the matrix. Particle sizes of the agglomerates were found to be around 160nm.

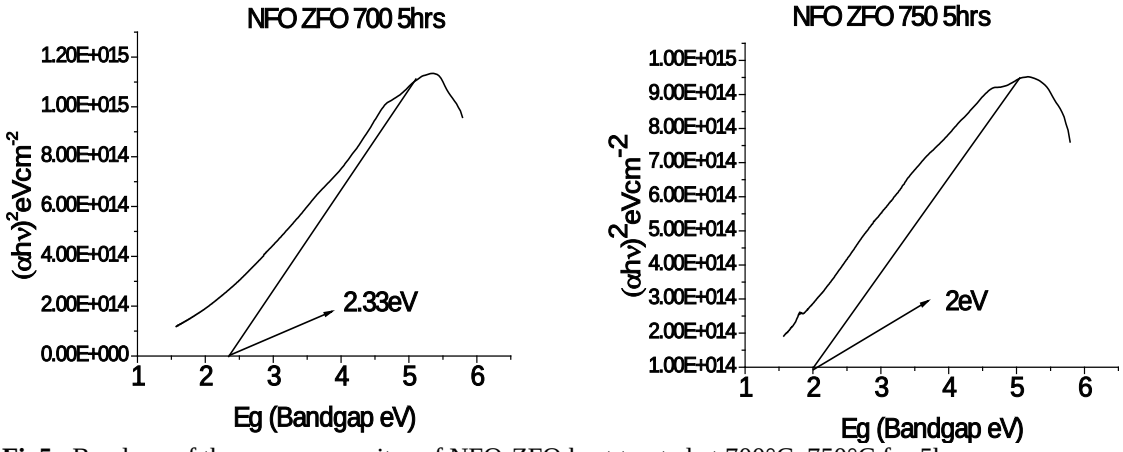


Fig5. Bandgap of the nanocomposites of NFO-ZFO heat treated at 700°C, 750°C for 5hours.

Bandgap of the nanocomposite of inverse spinel-normal spinel Nickel ferrite-Zince ferrite was calculated using Tauc relation [$(\alpha h\nu) = B(h\nu - E_g)^2$] from the UV-VIS spectra (Fig-5) at transmission mode within the scan range of (200-700) nm wavelength. Bandgap evaluated for the nanocomposite (2.33eV for NFO-ZFO 700 5hrs, 2eV for NFO-ZFO 750 5hrs) was found to lie in the energy band transition range for semiconductor materials. Bandgap of nanocrystalline Zinc ferrite was found to be about 2.7eV (Direct Eg) [6], while that of nanocrystalline Nickel ferrite was found to be around 5eV [7]. Thus, the bandgap evaluated was found to be close to direct bandgap of nanocrystalline Zinc ferrite. Thus, the material may have some potential applications in the field of catalysis (i.e. degradation of organic wastes or pollutants from industries, dyes) in the visible range and also applicable to remove iron based pollutant from water bodies using the magnetic property of the material.

3. Conclusions

Nanocomposite of spinel ferrites were synthesized using chemical coprecipitation route. Phase developed were identified by XRD analysis and crystallite size was calculated using Scherrer formula. Crystallite size of ZFO were found to be within 23.6 to 70.6 nm and for NFO 23.23-70.7nm. SEM studies reveal interconnected agglomerates with particle size about 160nm. Bandgap of the nanocomposites of NFO-ZFO were evaluated using Tauc relation and found to be 2eV and 2.33eV for 700^0C, 5hr and 750^0C, 5hr heat treatment. The prepared nanocomposites have bandgap close to semiconductor and can be applied as catalyst for decomposition of complex hydrocarbons; dyes in visible range coupled with removal of iron based polluting species from water bodies.

4. References

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