Influence of polymer matrix and magnetic field on the optical and electrical properties of fine particles of nickel ferrite

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Abstract   Polymer magnetic composite film based on fine nickel ferrite particles and poly vinyl alcohol has been prepared in the presence and absence of magnetic field. Various properties of the films such as morphology, electrical properties, and optical absorption reveal a clear effect of the presence of magnetic field of very low field strength (20 Oe) during gelation of polymer

Keywords   Nickel ferrite, fine particles, polymer matrix, optical and electrical properties

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1. Introduction

Nanostructured magnetic materials have been a subject of great scientific and technological interest [1–3] in recent times. Some of the interesting properties reported are superparamagnetism [4], enhanced coercivity [5], quantum tunneling of magnetization and giant magneto resistance [7]. Organic-inorganic composites have recently drawn attention of scientists all over the world due to its potential biomedical application [8]. It is reported [9,10] that arrangements of magnetic particles in the polymer based matrix play a major role in determining its magnetic properties. In compatibility of the matrix with magnetic particles is an important factor in connection with the absorption of the polymer on the surface of the filler [11].

Magnetic fine particles dispersed in various liquid media known as Ferro fluids, are materials of great interest for numerous physical and engineering applications [12,13]. The support, or matrix within which fine particles are synthesized or embedded plays an active role in determining their physical properties in addition to providing means of particle dispersion [14,15]. We report here preliminary investigation on optical, electrical and magnetic properties of nickel ferrite based magnetic polymer.

2. Sample preparation

Here we explored the advantage of synthesizing nickel ferrite $NiFe_2O_4$) particles by polyethylene glycol (PEG) route [14].

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Some of the possible reasons for employing PEG in the present study are : (i) PEG has a sharp melting point and decomposition temperature which are widely separated, (ii) PEG is known to be a good surfactant and a dispersant, which when employed may be beneficial in dispersion of the powders.
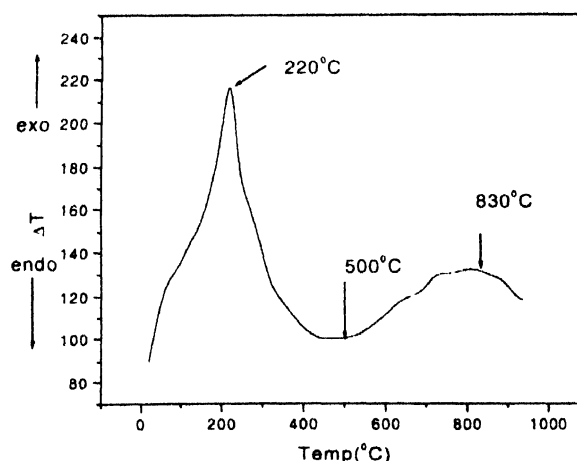

Figure 1. Differential thermographs of the precursor sample $NiFe_2O_4$

It is also reported that some polyols appear as crystal growth medium of particular interest in the synthesis of some oxides [15]. AR grade PEG (mol.wt. 600), α-Fe_2O_3 (99%) and NiO (99%) were used for the present investigation. After several trials, four times PEG was thoroughly mixed with stoichiometric

composition of nickel oxide and α-ferric oxide in a motor vessel and resultant solid was employed for differential thermal analysis using a Shimadzu DT-40 Thermal Analyzer. Ferrite particles were formed by two-stage heat treatment at 500°C for 1 hr and 830°C for 0.5 hr respectively as determined by the thermograph (Figure 1). The formation of monophasic $NiFe_2O_4$ was observed from the X-ray diffraction data. Ferro fluid (spec. 1) was prepared by dispersing ferrite particles in ethyl alcohol medium using ultrasonic bath. Ferro fluid thus prepared was mixed with 50% polyvinyl alcohol and water for casting freestanding film in the presence (spec. 2) and absence of magnetic field (spec. 3). These samples were employed for further characterization.

3. Experimental method

X-ray diffraction patterns were recorded in a Seifert XRD 3000 P Diffractometer using $Cu-K_\alpha$ radiation. The crystallite sizes of the magnetic phase was estimated from the broadening of the prominent diffraction lines using the Scherrer equation [16]

$$d = \frac{0.89\lambda}{\beta \cos\theta}$$ (1)

where λ is the wavelength of radiation, β is the line broadening (in radians), θ is the angle of diffraction and d is the particle size.

Optical absorption spectra of all specimens were taken in UV-1601 Shimadzu Spectrometer in the range 800 nm to 400 nm. Optical micrographs of ferrite particles in PVA film of thickness 0.1 cm were taken in Leica optical microscope at 600 magnification. DC electrical resistivity measurement as a function of reciprocal of temperature was carried out using Keithley 617 electrometer in the temperature range 300–153K in vacuum. Silver paint was applied on the two faces of magnetic composite film for electrical contact and ohmic contact was checked for the *V-I* characteristics. Saturation magnetization (M_s) and residual

Figure 2. Diffractogram XRD of nickel ferrite produced by PEG route.

magnetization (M_r) of the magnetic composite films were taken in a PAR vibrating sample Magnetometer at room temperature.

4. Results and discussion

Figure 2 shows the XRD pattern of the polycrystalline nickel ferrite powder prepared by two-stage heat treatment at 500°C and 830°C. Final temperature of crystallization is considerably lower than conventional ceramic technique of the order ~12500°C.

Figure 1 shows the differential thermographs of the precursor sample having two exothermic peaks at 220°C and at 830°C The lower peak at 220°C corresponds to the formation of γ-Fe_2O_3. γ-Fe_2O_3 later reacts with NiO to form $NiFe_2O_4$ through solid state reaction

$$NiO + \gamma\text{-}Fe_2O_3 = NiFe_2O_4$$
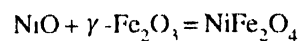
Particle size of the ferrite phase was determined by using the Scherer equation having mean diameter 25 nm. Figures 3a and 3b show optical micrographs of the polymer composite films. Agglomeration of the ferrite particles (dark phase) in the polymer matrix is evident from the optical micrographs. The micrograph of the specimen (3) shows interconnected type of morphology
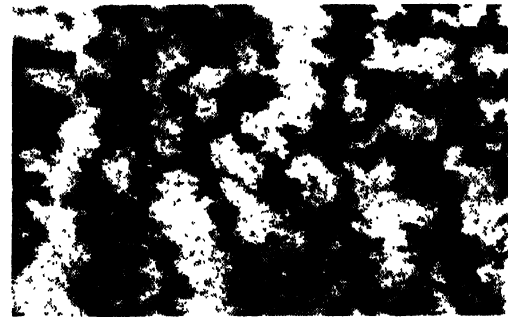

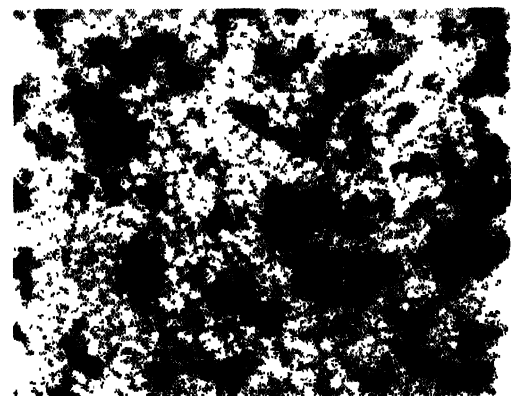**Figure 3a.** Optical micrograph of Spec 3
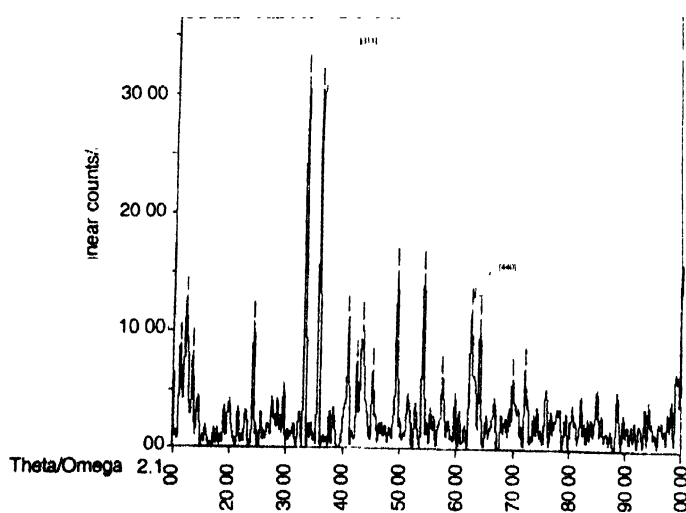

Figure 3b. Optical micrograph of Spec 2

as shown in Figure 3a. This specimen was cast in the absence of the magnetic field. This microstructure can be characterized in terms of a fractal dimension [17]. Characterization of the aforesaid microstructure in terms of fractal dimension will be carried out in future. Fractal growth of barium ferrite phase in silica matrix has been reported earlier [18] by the present authors. On the other

hand we see dispersion of macro clusters of ferrite particles in the polymer film, which was cast in the presence of very low magnetic field of strength 20 Oe.

We carried out optical absorption for the undoped and doped materials in the UV-visible region. Figure 4 shows optical absorption of all the specimens under present investigation in the region λ = 400–800 nm. A distinct change of the optical
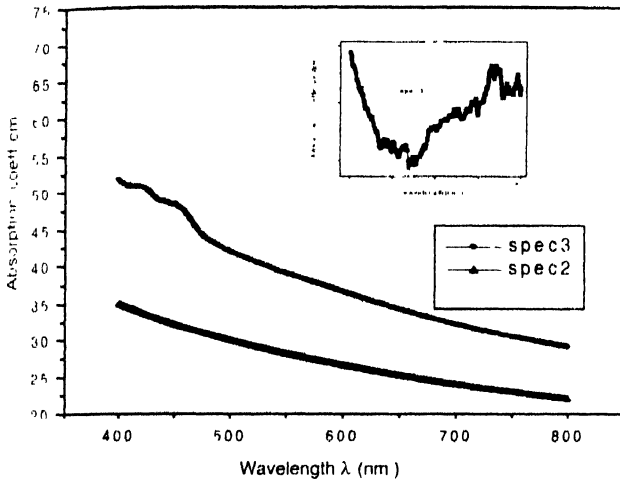

Figure 4.

absorption pattern of magnetic composite films compared to ferro fluid is evident from the optical absorption spectrum. The absorption coefficient was determined from the absorbance vs wavelength (λ) traces for powder and films. The absorption coefficient (α) is written as [19]

$$\alpha h\nu = A\left(h\nu - E_g\right)^n \qquad (2)$$

where E_g is the optical band gap corresponding to a particular transition occurring in a film and m characterizes the nature of transition. The value of m may be 1/2, 2, 3/2 and 3 corresponding to the allowed direct, allowed indirect, forbidden direct, and forbidden indirect transitions respectively [20]. To determine band gap and the nature of the transition we proceed as follow –

From (2) we obtain

$$\frac{d[\ln(\alpha h\nu)]}{d(h\nu)} \qquad \frac{m_i}{\left(h\nu - E_{g_i}\right)}$$

which predicts a divergence at an energy value, E_g, where a transition takes place. Plot of the derivative spectra for ferrite powders and ferrite based PVA films are shown in Figures 5(a) and 5(b) respectively. The discontinuities in the plots are observed at 1.58,1.99 and 1.63 eV for spec. 1, spec. 2, and spec. 3 respectively. The nature of transition for all the three specimens has been determined from the slope (m) of $\ln(\alpha h\nu)$ vs $\ln(h\nu - E_g)$ graph. The m values obtained in the range 0.45 –

0.49, which is close to 0.5 (Allowed direct transition). The exact values of band gaps corresponding to the m values mentioned above were obtained from $(\alpha h\nu)^{1/m}$ vs $h\nu$ plot. Band gap (E_g) along with the m values are shown in Table 1.
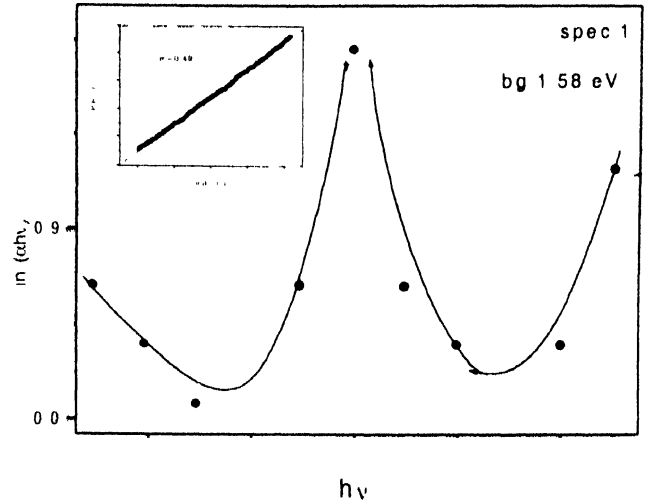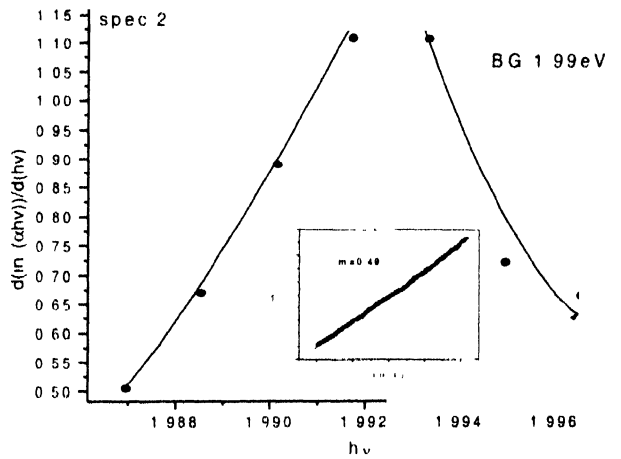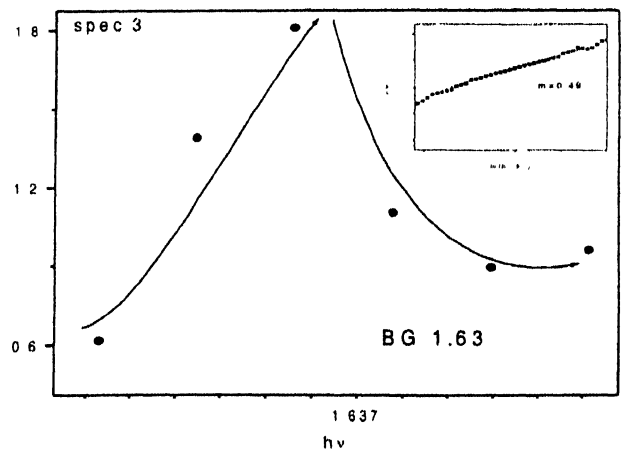

Figure 5(a).

Figure 5(b)(1).

Figure 5(b)(2).

E_g value of (1.64–2.01) eV of nickel ferrite is comparable to isoelectric structured compound γ -Fe_2O_3 (2 eV) in PVA matrix

Table 1.

Specimen	Band gap (eV)	m values
Spec 1	1 64	0 49
Spec 2	2 01	0 42
Spec. 3	1 76	0 49

[21] and $ZnFe_2O_4$ (1.25–1.9 eV) [22], depending upon the volume fraction of the ferrite phase in the silica matrix. Enhancement of band gap for ferrite particles embedded in polymer matrix is probably due to the confinement of the nanoparticles in polymer matrix and interaction between particle and matrix.

Figure 6 shows the resistivity variation as a function of reciprocal of temperature. It is interesting to note that a very low magnetic field (20 orested) dispersed the ferrite particles in the polymer matrix and electrical percolation is lost in the specimen 2. Conductivity mechanism of the ferrite particles embedded in polymer matrix will be discussed elsewhere.
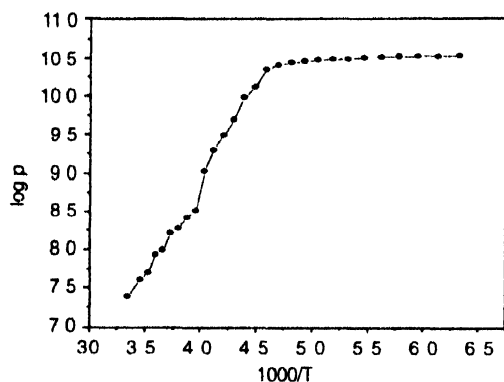

Figure 6.

Figure 7 shows the variation of magnetization with the magnetic field. It is interesting to note that saturation magnetic field for spec. 2 is less than spec. 3. This can be explained by the preferred orientation of the easy axis of magnetization of the ferrite particles in polymer film, which was cast in presence of the magnetic field.
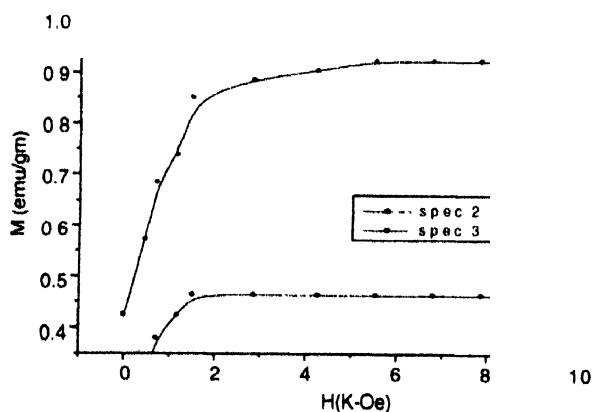

Figure 7.

5. Conclusion

In conclusion we have been able to synthesize nickel ferrite by PEG route at considerably low temperature and embed corresponding phase in a suitable polymer matrix. Effects of polymer matrix and magnetic field on various physical properties such as microstructure, optical, magnetic and electrical are quite evident from present investigation. In principle the macroscopic parameters of the composite magneto-polymers are influenced by the interactions between the filler and the matrix.

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