Structural and Magnetic Analysis on Spinel (NiFe$_2$O$_4$) Prepared By Sol Gel Process at Different Calcinations Temperatures

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Abstract: *NiFe$_2$O$_4$ nanoparticles (NFO) prepared by sol gel process based on the citric acid at room temperature. The structure, microstructure, and magnetic properties of the NFO nanoparticles were studied under the effect of calcinations temperature. The prepared nanoparticles were characterized by X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR), transmission electron microscope (TEM) and vibrating sample magnetometer (VSM) studies were carried out to investigate the formation of crystalline nanosized (NFO) spinel.*
Keywords*: nanostructures, sol gel process, Spinal ferrites, VSM, XRD.*

I.   Introduction

The performances of nano-sized NiFe$_2$O$_4$ spinel materials have been investigated with profound interest in past few years. Where, ferrites are one basic but important group of magnetic materials, in which spinel-type ferrites (MFe$_2$O$_4$, M = Fe, Co, Ni, etc.) have a considerable attention. [1,2] The magnetic ferrites materials have been intensively progressed due to their unique properties and their various applications as a high density magnetic recording, drug delivery and biocompatible magnetic nanoparticles for cancer treatment [3-5]. In general, spinal ferrite can be formed by the traditional methods, which is regarded as simple and suitable for mass production [6,7].

However, these methods are limited by the evaporation of the volatile component and presence different phases during high-temperature processing. The sol–gel process is an alternative method to preparing ferrite materials that has been widely studied in recent years [8]. The sol–gel process has many advantages are well known such as low temperature process, gives homogeneous mixtures in the final composition, high purity [9,10].

Here we show that, with ambient precautions, trend of calcination can be affected in the densification behavior for the prepared oxides. Nickel as an essential dopent element in ferrite-based nanoparticles is known to have stimulatory effects on spinal formation [11]

In this work, the prepared nano-sized spinal was characterized and magnetic studies were performed to analyze its feasibility as an implant material.

II.   Experimental work

2.1. Materials

All the chemicals used for synthesis were of analytical grade. Nickel nitrate (Ni(NO$_3$)$_2$ -6H$_2$O), ferric nitrate(Fe(NO$_3$)$_3$ -9H$_2$O), citric acid (C$_6$H$_8$O$_7$.H$_2$O), ethylene glycol, and all chemicals were used without any further purifications.

2.2. Synthesis of nickel ferrite (NFO) nanoparticles

NFO nanoparticles were done by sol–gel method through hydrolysis and condensation. Cobalt ferrite nano-particle was prepared with the following steps:(i) The nitrates of (Fe^{3+}:Ni^{2+}ions, 2:1 molar ratio) were dissolved individually in ethylene glycol under magnetic stirring for 30 min. (ii) Added a certain amount of citric acid to the previous solutions (iii) added both solutions to each other and stirred at 80°C until a clear and viscous sol was obtained (iv) the viscous sol was dried at150^{o}C for 10h; and (iiv) the dried gel was calcined at 400°C for 4h in air.

2.3. Characterization

The structural characteristics of the sample were characterized by X-ray diffraction (XRD). The average crystallite size was calculated from the most intense peak (311) by using the Scherrer's formula [12].

$$G = \frac{k\,\lambda}{D\,cos(\theta)}$$

where k = 0.9 is the Scherrer constant, λ = 1.54056Å is the wavelength of X-ray, and D is the full width at half maximum intensity (FWHM) of the peak.

TEM is used to elucidate the microstructure of the prepared materials and give approximation of the particles size distribution. FTIR spectra technique was used to characterize the chemical structure of materials. The magnetic analysis for the prepared nanoparticles was determined by using vibrating sample magnetometer (VSM).

III.   Result and discussion

3.1 Structural analysis-XRD

Fig. 1 represents the XRD pattern of the prepared nickel ferrite (NFO). The XRD for (NFO) prepared by sol-gel and calcined at different temperature shows good behavior for poly-crystalline materials. All peaks of the prepared samples and its position at 2θ scale are completely compatible with the characteristic peaks of cubic spinel $NiFe_2O_4$ and they are matched with the XRD card no.86-2267. As seen from Fig.1 there is no other peaks related to nickel oxide, iron oxide or other phases which indicate that we have pure cubic spinel $NiFe_2O_4$ phase.

By increasing the calcination for the prepared samples from 400°C up to 800°C, the XRD peaks become sharper, narrower, and the crystallization of NFO is improved and the consequent crystalline grains grow,[13] as shown in Table 1.The crystallite size of NFO was found to be in the nano-sized and increases from 19 to 26 nm as the calcination temperature increase.
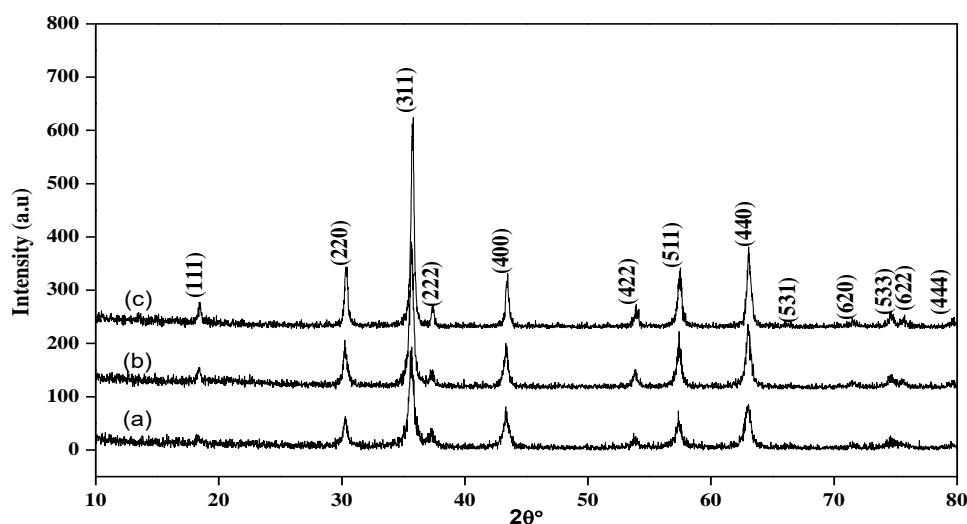

Fig.1. X-ray diffraction (XRD) pattern of NFO nanoparticles prepared using sol–gel process and calcined at different temperature for 4h in air, (a) 400°C, (b) 600°C and (c) 800°C.

3.2 transmission electron microscopy (TEM)

Fig.2 shows the TEM images of NFO-EG powder calcined in air for 4h at 800°C. The microstructure study of NFO shows that NFO prepared using sol-gel method and calcined in air for 4 h has uniform spherical shape as presented in Fig. 2a. NFO particles size that estimated from TEM was in the range of 20 to 40 nm that agree with the particle size estimated from XRD. Fig. 2b shows larger particles of NFO and dark color which can be attributed to the agglomeration of fine particles of NFO.
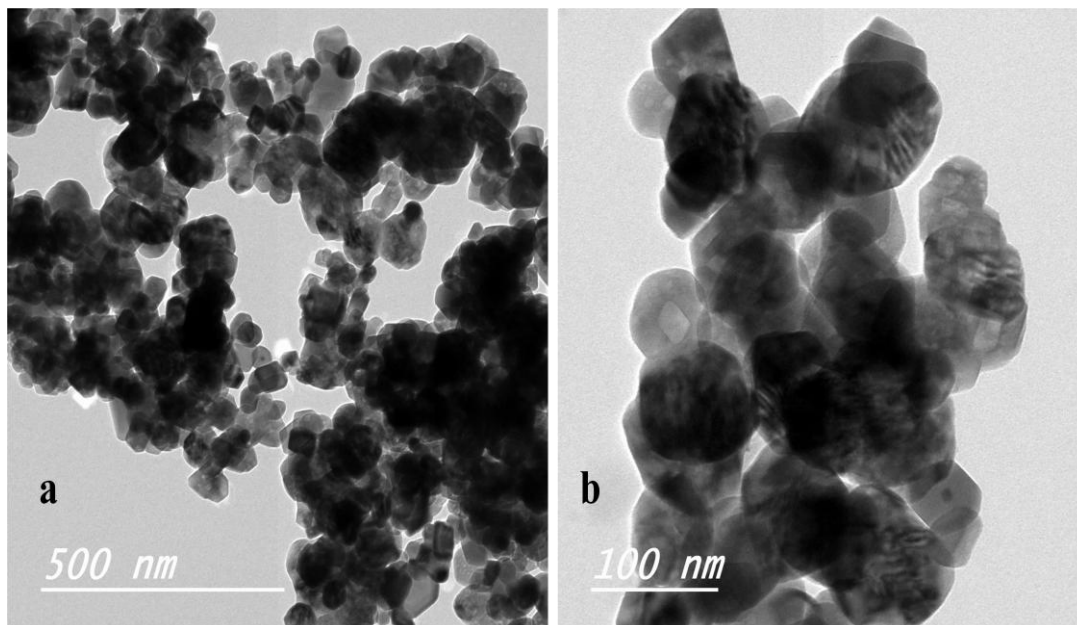
Fig.2 TEM Of NFO calcined in air for 4 h at 800 °C

3.3 FTIR analysis

Fig.3 shows the FTIR spectra of nickel ferrite (NFO). Nickel ferrite belongs to the inverse spinel structure group, so it has a distribution of cations between octahedral and tetrahedral sites and hence the two absorption bands at 421 and 592 cm⁻¹ can be assigned to the stretching vibration frequency of the metal-oxygen at the octahedral site and tetrahedral site respectively. [14,15] The absorption band at 941 and 1020 cm⁻¹ may be attributed to the bending vibration of C-H and stretching vibration of C-N. 1020 cm⁻¹ may be corresponding to the nitrate traces [16]. The band at 1428 cm⁻¹ was assigned to symmetric vibration (COO-) of the carboxylate group bonded to the nanoparticle surface. The 1636 cm⁻¹ band is due to the deformation mode of adsorbed water, assigned to the bending vibration. The absorption band of symmetric and asymmetric vibrations of CH_2 groups appeared at 2926 and 2853 cm⁻¹, respectively, they can be attributed to organic residues. The band at 3442 cm⁻¹ can be assigned to O-H stretching vibration interacting through H bonds that originate from moisture content in the sample [17].
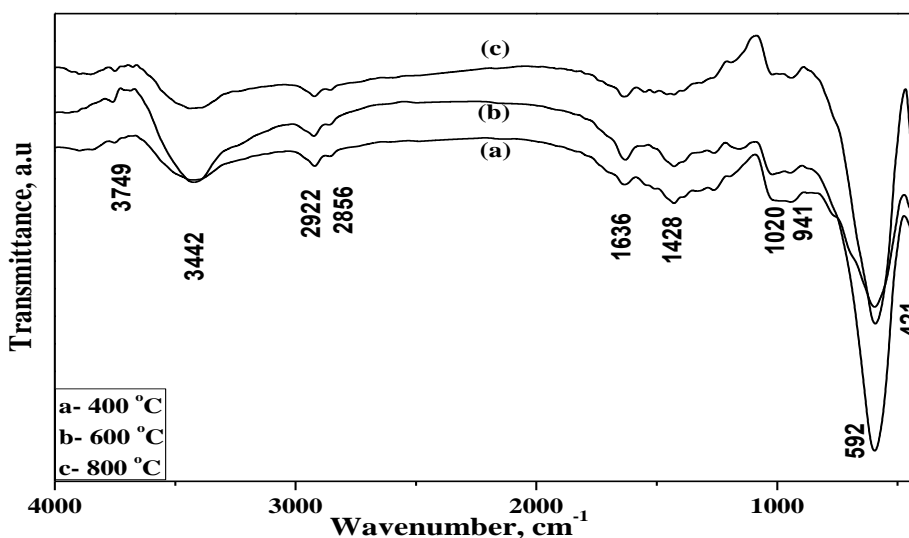

Fig. 3 FTIR spectra of NFO calcined at different temperature for 4h in air (a) 400, (b) 600 and (c) 800 °C.

3.4 Magnetic properties

Fig.4 shows the hysteresis loop of NFO performed at rome temperature by VSM under applying magnetic field range ±20KOe. The different magnetic parameter that estimated from the M-H curve like saturation magnetization, coercivity and squareness are summarized in Table 1. Nickel-ferrite (NFO) is known as a cubic ferromagnetic material with inverse spinel structure in which half of Fe^{3+} occupy the tetrahedral A

sites and the other half participate the octahedral B sites with Ni^{2+}. Its ferromagnetism arises from magnetic moment of anti-parallel spins between (Fe^{3+} and Ni^{2+}) ions at the octahedral sites and Fe^{3+} ions at tetrahedral sites.

Fig.4 demonstrates that NFO calcined at different temperature has a saturated magnetic hysteresis loop with increasing in saturation magnetization from 36 to 46.5 emu/g as the calcination temperature increases from 400 to 800°C. This behavior is expected because the increasing in calcination temperature leads to increase in particle size and magnetocrystalline anisotropy.

It can be seen that the saturation magnetization (M_s) of all samples is less than that of bulk NFO (55 emu/g). These small values can be attributed to the spin canting at the surface of nanopowder. Also coercivity of NFO increases as the calcination temperature increases and it has a relatively high values ranging from 120 to 197 Oe. The increasing in coercivity with particle size can be interpreted as that the particle of NFO calcined at different temperature is consist from single domain. It is well known that the rotation of domain requires high energy than the motion of domain walls and hence the demagnetized field (coercivity) of NFO increases as the particle size increases under the critical size of domain.

Table 1 shows the squareness (M_r/M_s) values of NFO and it shows a small values ranging from 0.07 to 0.17. These small values can be attributed to the noninteracting single domain particles with uniaxial magnetocrystalline anisotropy.
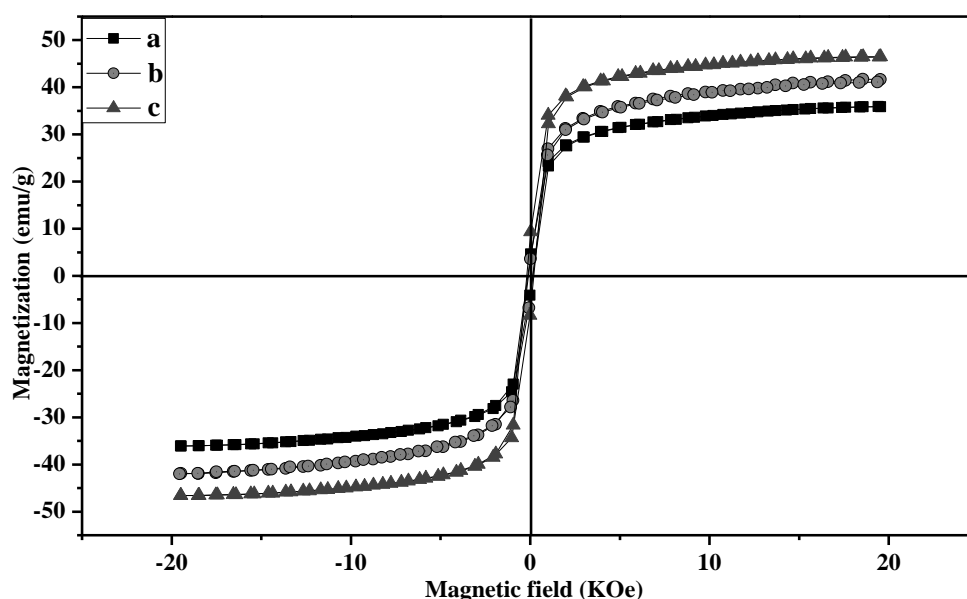

Fig.4 Hystersis loop Of NFO calcined in air for 4h at different temperature (a) 400, (b)600 and (c) 800°C.

Table 1 shows grain size, saturation magnetization (M_s), remanent magnetization, coercive field (H_c) and reduced magnetization (M_r/M_s) of NFO

Calcinations Temperature °C	Grain size nm	M_s emu/g	M_r emu/g	H_c Oe	M_r/M_s
400	19 nm	36.007	3.8304	139.41	0.106
600	24 nm	41.858	3.0569	120.51	0.07
800	26 nm	46.519	8.0561	197.5	0.17

IV.   Conclusion

The nano-sizes NFO prepared by sol gel process and calcined at different temperature ranging from 19 to 26 were investigated. Saturation magnetization and remanant magnetization were increased from 36 to 46.5 and 3.8 to 8, respectively due to the enhancement in the magnetocrystalline of the prepared ferrites as the calcination temperature increased from 400 to 800 oC due to the increment.

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