

Spectroscopy, Structural, and Optical Investigations of NiFe₂O₄ Ferrite

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ABSTRACT— Ni ferrite crystalline material is synthesized using a sol-gel method at two different temperatures. The vibrational and stretching modes, crystalline phase, size distribution and morphology of the products are investigated via Raman back-scattering and Fourier transform infrared (FTIR) spectroscopy, XRD and FESEM, respectively. Vibrational modes of spinel ferrite are observed at Raman and FTIR spectra. Group theory phonon analysis reveals five Raman active modes for the molecular system. However, in the present investigation, four Raman modes are identified in the inelastic Stokes region of the recorded Raman scattering spectra. Also, the results of the present study reveals that the sizes of the synthesized particles were increased and crystalline structures were completed by increasing the temperature.

KEYWORDS: spinel ferrite, sol-gel method, Back-scattering Raman spectroscopy, FTIR Spectroscopy.

I. INTRODUCTION

Ferrites are a very important group of magnetic materials due to their extensive use in a wide range of applications, such as ferrofluids, radar absorbing coatings, waveguides in the gigahertz region, biomedical and clinical devices, magnetic resonance imaging, oxyfuel technology, gas sensors, for the fabrication of magnetic cores of read/write heads for high-speed digital tapes or for disc recording [1-5].

Spinel ferrites are a large important class of materials with the general formula MFe₂O₄,

where M is a divalent cation. Nickel ferrite, NiFe₂O₄ (NFO), is an inverse spinel in which the tetrahedral sites (A) are occupied by Fe²⁺ and Ni²⁺ ions [6, 7].

NFO is one of the most attracting material of spinel ferrite due to their interesting and important properties such as high electrical resistivity, large expansion coefficient, high saturation magnetization, high permeability and low eddy current loss, etc. In view of these properties, it is used as one of the best microwave absorber materials. This type of ferrites is also used in various forms such as nanoparticles, nanowires, nanotubes, thin films and so on [4, 8]. Several techniques are used for the preparation of ferrite particles, such as citric acid combustion method, sol-gel method, organic gel thermal decomposition method, hydrothermal method, co-precipitation method [9-14]. Sol-gel is a simple method that has advantages, such as simple preparation route, with precisely controlled relative stoichiometric ratios, which produces ultra-fine and homogeneous powders [14].

In the present work, NFO spinel ferrite was prepared by sol-gel method. Consequently the products are characterized by back-scattering Raman spectroscopy, FTIR spectroscopy, X-ray diffraction (XRD) and field emission scanning electron microscope (FESEM).

II. EXPERIMENTAL PROCEDURES

The chemical materials nickel nitrate, iron nitrate and citric acid were used as raw

materials to prepare nickel ferrite sample and citric acid is used for chelating metallic ions. The preparation process is described as follows; first nitrate salt of metallic ions and citric acid were dissolved in deionized water, so that the molar ratio of Ni:Fe: citric acid was reached to 1:2:3. In this step, the solution was continuously stirred at 90 °C for 6 h.

Then the above mixture was kept at 100 °C for 24 h until all the solvent was evaporated. The dried gel, xerogel, then milled for 3 h in a planetary mill and calcined at different temperatures of 950 (S9), 1050 (S10) °C. The calcinations schedule of the sample was as follows: from room temperature to 400 °C and staying at 400 °C for 1.5 h, then 400 °C to 950 or 1050 °C and staying at final temperature for 4 h. The heat increasing rate of furnace was 2 °C/min. The final products were black powders.

III. RESULTS AND DISCUSSION

A. Raman spectra analysis

A typical set of recorded Raman spectra of the samples were shown in Fig. 1. These spectra were collected at the Spectroscopy Laboratory, Atomic and Molecular Group, Physics Department, Tarbiat Modares University by using a Thermo Nicolet Almega dispersive micro-Raman scattering spectrometer operating by a 532 nm line as the second harmonic of a Nd:YLF laser.

Nickel ferrite has inverse spinel structure, prototype symmetry O_h^7 and space group of $Fd3m$. Based on group theory, spinel type of ferrites has five Raman active modes. In following, the typical appearance of these modes is shown [15, 16]:

$$A_{1g} + E_g + 3F_{2g}$$

According to the Fig. 1(a), these modes have appeared at 404, 486, 559 and 698 cm⁻¹ corresponding to E_g , F_{2g} (2), F_{2g} (3) and A_{1g} , respectively.

Because of the wavelength used, F_{2g} (1) has not been observed in the recorded Raman spectra. It should be noted that Raman peaks over the region of 660-720 cm⁻¹ represent the modes of tetrahedral group (T-site) and those in the 460-660 cm⁻¹ region correspond to the modes of octahedral group (O-site) of ferrites [9, 16, 17].

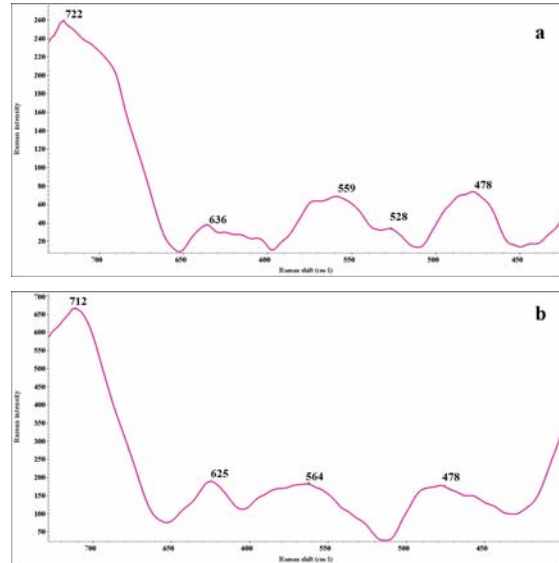


Fig. 1 Raman spectra of the synthesized samples: (a) sample S9; (b) sample S10.

Also in Fig. 1(b), the modes have been appearing at 399, 484, 564 and 709 cm⁻¹ respectively.

Table 1 Raman mode labels for sample S9

Mode label	Wavenumber (cm ⁻¹)	Shoulder (cm ⁻¹)
E_g	420	-
F_{2g} (2)	478	460
F_{2g} (3)	559	528
A_g	722	700

The difference between Raman spectra of the samples is the appearance of some additional peaks in the Raman spectrum of sample S9 in comparison to the other Raman spectrum related to sample S10. Also increase in the intensity of the peaks and illumination of some other peaks were observed at 500-550 cm⁻¹ and 600-650 cm⁻¹ spectral regions. This is due to the increasing of grain sizes and accordingly more crystallinity of the structure.

Most of the observed modes have shoulder peaks with lower wavenumbers. A possible explanation of these extra modes is the inversion of the NFO lattice. The existence of both Fe^{3+} and Ni^{2+} occupying the octahedral sites which leads to separate vibrational frequencies for the NiO_6 and FeO_6 octahedra.

Table 2 Raman mode labels for sample S10

Mode label	Wavenumber (cm ⁻¹)	Shoulder (cm ⁻¹)
E_g	399	390
$F_{2g}(2)$	478	458
$F_{2g}(3)$	564	550
A_g	712	-

B. FTIR spectra analysis

The recorded FTIR spectra for the synthesized samples are shown in Fig. 2. Since spinel ferrites have four IR active bands that are shown as 4F1u. They are in the spectral region ν_1 (630-560 cm⁻¹), ν_2 (525-390 cm⁻¹), ν_3 (380-335 cm⁻¹) and ν_4 (300-200 cm⁻¹). Two of the bands reported and found in the far-IR region have not been observed [10, 14, 15].

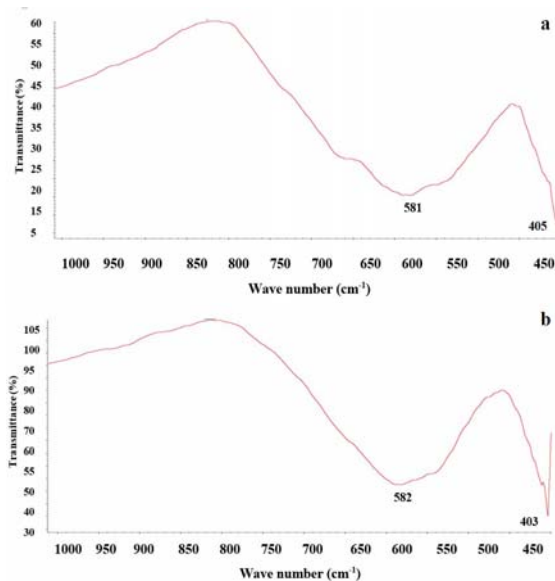


Fig. 2 FTIR spectra for the synthesized samples: (a) sample S9 and (b) sample S10.

By inspecting Fig. 2(a), two modes have appeared at 405 and 581 cm⁻¹ corresponding to ν_1 and ν_2 , respectively. These bands are assigned to the vibrations of the tetrahedron and octahedron for the trivalent (Fe^{3+}) cation,

respectively. Also in Fig. 2(b), two vibrational modes have appeared at 403 and 582 cm⁻¹. First mode is attributed to the stretching vibrations of tetrahedrally coordinated $\text{Fe}^{3+}-\text{O}^{2-}$ bonds and second mode is attributed to the metal oxygen vibrations in the octahedral sites.

The difference in band positions for tetrahedral and octahedral complexes is due to the difference in values of $\text{Fe}^{3+}-\text{O}^{2-}$ bond distances.

A comparison between the spectra of the synthesized samples shows that some additional modes in the sample S9 are due to the presence of impurities such as Fe_2O_3 . Also, the intensity of the observed modes are greater for the sample synthesized at 1050 °C (the sample S10) and with narrower widths, which is due to the more crystallinity structure of the Ni ferrite in this sample. Also in the Fig. 2(a), additional peak is observed in the region of 600-700 cm⁻¹ which is related to the deficiency of the structure. The peak width decreases with increasing temperature and transmittance intensity is increased and this can be attributed to an increase of the grain sizes.

C. X-Ray diffraction (XRD) analysis

The phase structure and purity of the synthesized particles were identified by an X-ray diffractometer (X'Pert MPD, Philips), with $\text{Cu K}\alpha$ radiation.

Fig. 3 shows the recorded XRD patterns for the two synthesized samples of NFO. These patterns exhibit the reflection planes as shown in table 2.

All peaks are reasonably of sharp high intensity revealing high crystallinity of the synthesized samples. The XRD patterns clearly show that the pattern related to the sample S9 has some extra peaks. The centers of these peaks are at $2\theta = 33.14$ and 49.40 attributed to Fe_2O_3 structure. Also, peaks for the sample S10 are sharper and more intensified. It shows that crystal structure is completely formed in this sample and the

crystalline phase of NFO is determined with the face centered cubic (FCC) structure.

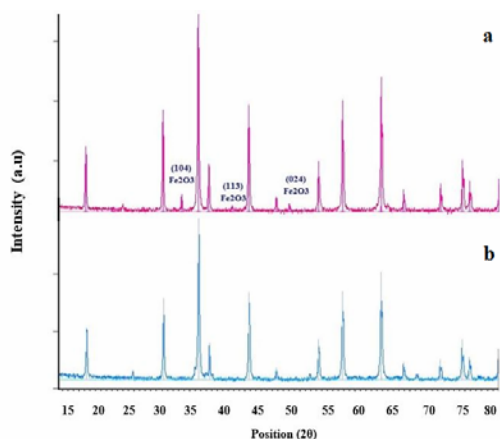


Fig. 3 The XRD patterns for the synthesized samples: a) sample S9, and (b) sample S10.

Table 2 The reflection planes in crystal lattice of NFO

Miller index	Position (2θ)	Miller index	Position (2θ)
(111)	18.34	(511)	57.35
(220)	30.26	(440)	62.99
(311)	35.65	(620)	71.5
(222)	37.30	(533)	74.56
(400)	43.34	(622)	75.58
(422)	53.80	(444)	79.58

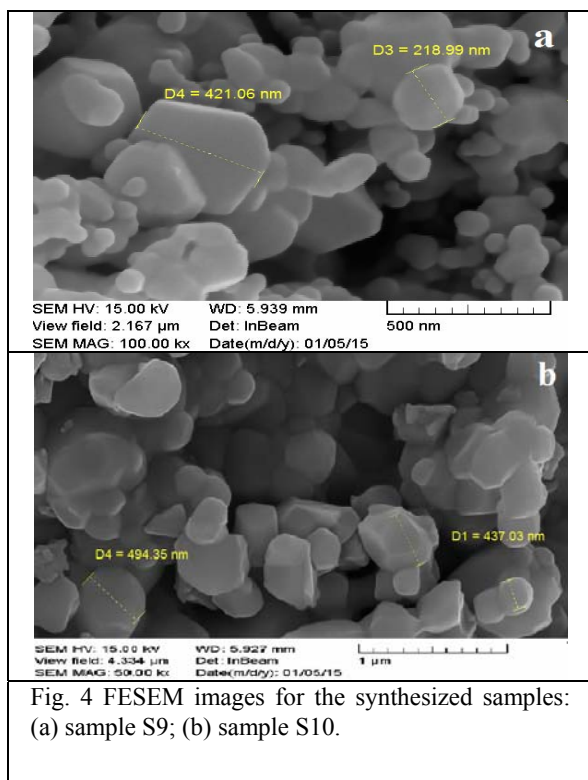


Fig. 4 FESEM images for the synthesized samples: (a) sample S9; (b) sample S10.

D. Field Emission scanning electron microscopy (FESEM)

Fig. 4 shows the FESEM images of the NFO at different temperatures. The images identify the following details: particle sizes have increased by increasing the temperature and their appearance shapes clearly shows that the best crystal structure is achieved at 1050 °C and the tetrahedron and octahedron structures are the dominant structures. Also the particles size distribution is almost uniform.

IV. CONCLUSION

NiFe₂O₄ was synthesized by the sol-gel method and calcined at two different temperatures of 950 and 1050 °C. According to group theory analysis five Raman active modes should be identified in the inelastic Stokes Raman scattering region. However, this research identified four, out of five, Raman peaks for the synthesized samples of the spinel ferrite.

Also FTIR spectra exhibited vibrational modes corresponding to metal-oxygen bonding. XRD pattern of NFO was identical and matched by the reference pattern present in the Standard X-ray Diffraction Powder Patterns. But pattern of sample S9 had addition peak corresponding to Fe₂O₃ structure. Finally the FESEM images show particle size distribution and morphology of NFO particles.

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