

# Optical and Structural Analysis of the MgFe<sub>2</sub>O<sub>4</sub> Nanoparticles, Synthesized By the Solid-State Reaction of Inorganic Precursor Route.

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## Abstract:

**Keywords:** Solid-state reaction of inorganic precursor method, FTIR, XRD, Raman spectroscopy, Magnesium ferrite, FESEM

In this study the result obtained from different characterizations for the MgFe<sub>2</sub>O<sub>4</sub> nanoparticles by solid state reaction of inorganic precursor's technique. Structural properties are carried out by using X-ray diffraction (XRD) technique and then formation of spinel MgFe<sub>2</sub>O<sub>4</sub> structure is confirmed by Fourier transform infrared spectroscopy (FTIR). The XRD of the powder sample was done at room temperature which gives the lattice parameter of the sample. The cations distribution is also confirmed by IR spectroscopy and Raman spectroscopy. An FTIR spectrum of the calcined samples at 800 c, gives the two strong absorption bands ( $\nu_1$  and  $\nu_2$ ) which are the characteristic bands of the spinel MgFe<sub>2</sub>O<sub>4</sub>. The  $\nu_1$  is high band due to the stretching vibrations of the Mg and O bonds in tetrahedral site while the low band  $\nu_2$  is appeared due to the bending vibration of the Mg-O bonds in octahedral site, these bands are appeared due to the different bond lengths in each sites. The local deformation takes place due to the presence of Fe<sup>2+</sup> cations at octahedral site, known as Jahn-Teller effect. The morphology of the nanoparticles is observed by ZEISS field emission scanning electron microscopy at BIT Meshra.

## 1. Introduction

MgFe<sub>2</sub>O<sub>4</sub> nano particles have attracted substantial attention due to its uses in various applications in research, photo catalyst, optoelectronics[29], magneto electronics, spintronics, anode materials and technology. The phase formation of nanocrystalline spinel ferrites plays an important role to determine, its physical properties like structural, optical and magnetic etc. Magnesium spinel ferrites (MgFe<sub>2</sub>O<sub>4</sub>) are also used widely as a gas sensor, humidity sensor and device with its n-type semiconducting material property. It is a soft magnetic material having cubic crystal system. Spinel ferrites also play a significant role in microwave control components such as circulators, isolators and phase shifters [1]. Among different ferrites, magnesium ferrite (MgFe<sub>2</sub>O<sub>4</sub>) enjoys a special attention because of its vast applications in high-density recording media, heterogeneous catalysis[30], adsorption, sensors and magnetic technologies. Nanoparticles of MgFe<sub>2</sub>O<sub>4</sub> have good photoelectrical properties [2], [3], [4]. The physical and chemical methods widely used in the synthesis of nano-ferrites are ball-milling, sol-gel, co-precipitation and hydrothermal methods [5], [6], [7], [8]. The choice of synthesis in this present work is a fundamental step in obtaining the desired characteristics in the final product. The resultant product must be pure with essential particle size and low aggregation and agglomeration, in addition to achieving low production cost. In this way, the solid state reaction of inorganic precursors processing method has been the subject of great interest in recent years. Among the various routes, this method yields more promising results in the synthesis of ultrafine particles at a fairly low temperature [4], [9] [10]. This work describes the study of MgFe<sub>2</sub>O<sub>4</sub> ferrite synthesized using solid state reaction of inorganic precursors processing method and the impact of nanoregime on its structural and optical properties.

## 2. Experimental

The compounds were prepared by solid-state reaction of inorganic precursors [13–15]. In this present work magnesium sulphate (MgSO<sub>4</sub>·7H<sub>2</sub>O), Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, NaOH and NaCl were mixed in a molar ratio (1:2:8:2) and grinding the all mixed compound in an agate mortar for about 30 min. During grinding the reaction occurs, the mixture became mushy and underwent gradual changes in colour from reddish violet for 5 min to finally brown after 10 min. This mixture was filtered with the help of 42 ashless filter paper rounding 100 circles and 7 cm in length, the mushy sample and then washed with deionizer water (700 ml) several times, for the removal of sodium chloride. Then the powders were dried at 90°C for 2 h in air oven, during this process the colour remains unchanged. The powders were then calcined at 800 C for 3 hrs. The proposed MgFe<sub>2</sub>O<sub>4</sub> system of the present study is synthesized by the solid state reaction of inorganic precursor's method as reported in earlier article [12]. The synthesized nanoparticles of MgFe<sub>2</sub>O<sub>4</sub> is characterized using X-ray diffraction (XRD)-PANalytical (Model: X'Pert PRO) for analyzing the phase, Field Emission Scanning Electron Microscopy (FESEM)- ZEISS, Fourier transform infrared spectroscopy (FTIR) ranging from 400 to 4000 cm<sup>-1</sup> for the presence of cations due to the local deformation in the lattice known as John-Teller effect [14], UV-VIS and Raman spectroscopy to reveal the vibrational and structural properties of materials. The grain size of the nanoferrite is determined using Scherrer's equation [10].

## 3. Result and discussion

### 3.1.x-ray diffraction (XRD) analysis

The XRD pattern of as-synthesized MgFe<sub>2</sub>O<sub>4</sub>-prepared through solid state reaction of inorganic precursor's method is shown in

Fig. 1. It is seen from Fig. 1 that the XRD pattern consists of well-resolved peaks, which confirms the polycrystalline and monophasic nature of the prepared material. In the Fig. 1 the major peaks observed at  $2\theta$  angles are 24.2, 33.18, 35.66, 40.9, 43.035, 49.52, 54.10, 62.50, 62.87 and 64.02 which correspond to the peaks corresponding to planes (1 1 1), (2 2 0), (1 3 1), (2 2 2), (0 4 0), (4 2 2), (5 1 1), (4 4 0), (6 2 0), (5 3 3) and (6 2 2) provide a clear evidence for the formation of spinel structure of the ferrite [14]. This observation matches well with those of earlier reporters [15,16]. It is also noted that the ferrite is free from residual  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase, which is normally expected during synthesis at relatively lower temperatures. The lattice parameter 'a' determined as 0.8376 nm matches well with JCPDS (73-2410) file for MgFe<sub>2</sub>O<sub>4</sub>. The volume of the unit cell for the ferrite is 0.586 nm<sup>3</sup>. The grain size of MgFe<sub>2</sub>O<sub>4</sub> is obtained by using Debye - Scherrer's formula as 35 nm. Bulk MgFe<sub>2</sub>O<sub>4</sub> is an inverse spinel with Mg<sup>2+</sup> ions occupying all the octahedral sites [17]. But according to our new cation distribution, Mg<sup>2+</sup> ions prefer both tetrahedral and octahedral sites, i.e. nano-MgFe<sub>2</sub>O<sub>4</sub> tends to exist as mixed spinel. An appreciable amount of Fe<sup>2+</sup> ion is also present in B-site. This degree of inversion is thus attributed to the method of synthesis and is ultimately an impact of nanoregime. The tetrahedral and octahedral bond lengths are determined as 0.1868 and 0.1982 nm, respectively. It is a known fact that the bond length of octahedral site is greater than the tetrahedral site.

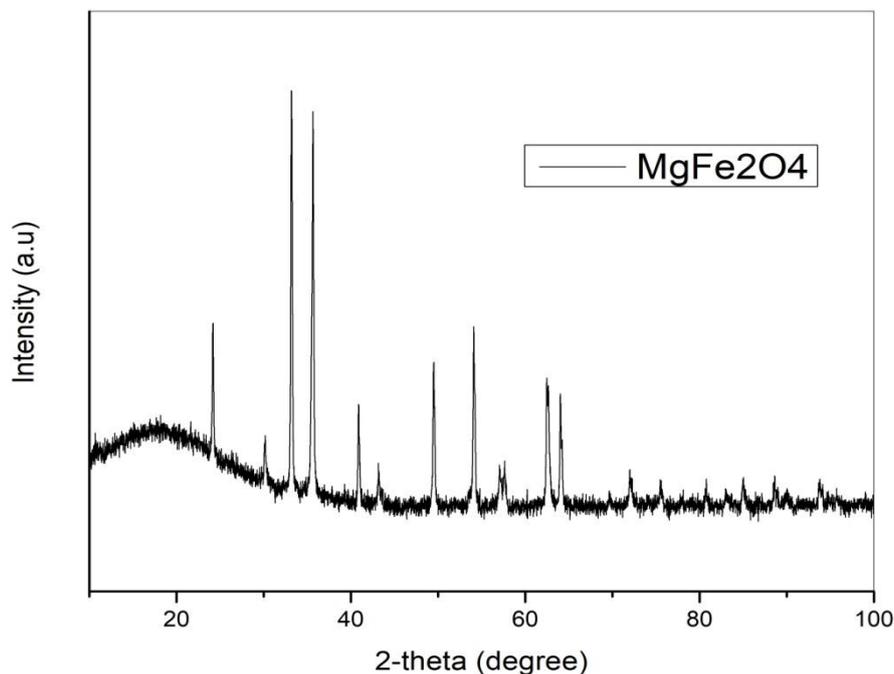
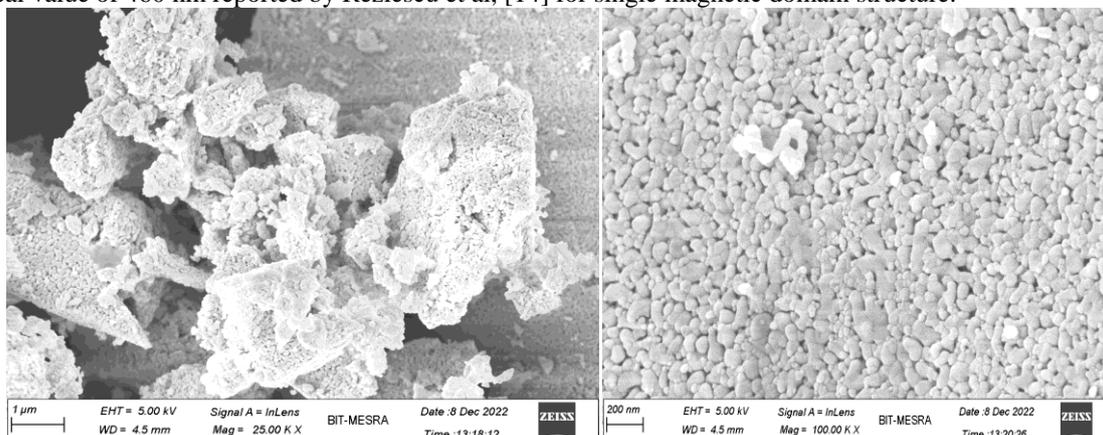
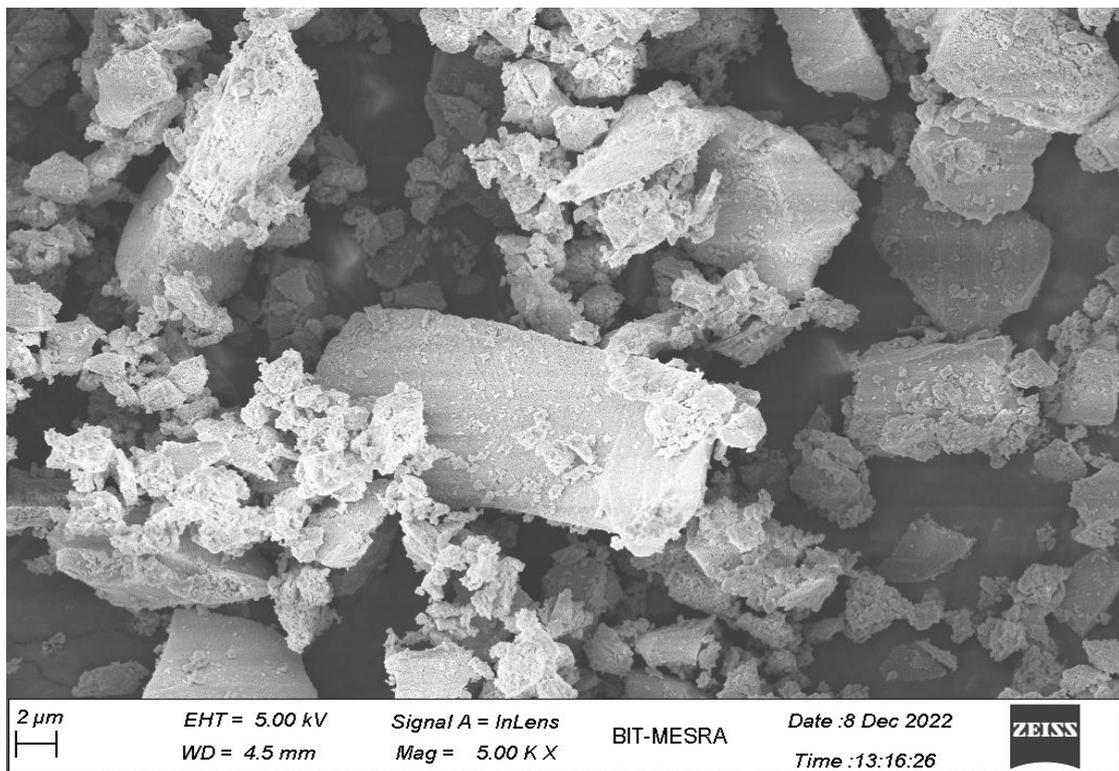


Fig- 1. XRD pattern of MgFe<sub>2</sub>O<sub>4</sub> powder

### 3.2. FESEM study

The microstructure of the nano-MgFe<sub>2</sub>O<sub>4</sub> powder is observed using the SEM micrographs, which is shown in Fig. 2(a–c). The micrographs show the presence of particles that are agglomerated together. A close inspection would reveal the presence of particles showing cubic faces[11]. The distribution of particles is uniform and it can be seen that the particles are well below the size of 100 nm, which supports our prediction of grain size determined by using Scherrer's formula. This value is much greater than the critical value of 460 nm reported by Rezlescu et al, [14] for single magnetic domain structure.

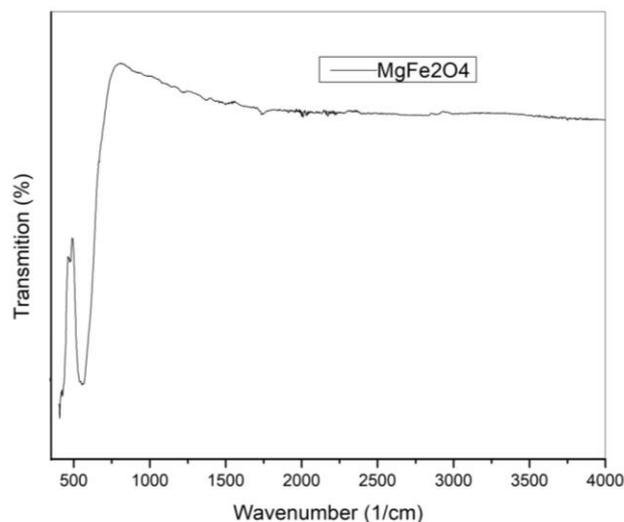




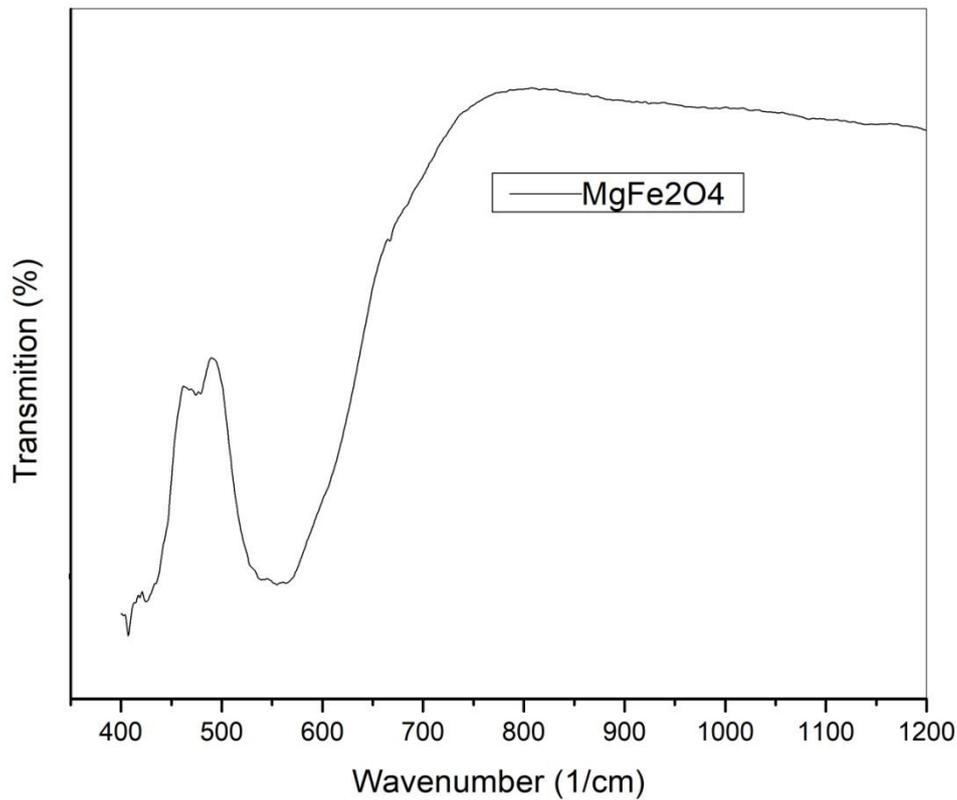
**Fig- 2. FESEM image of MgFe<sub>2</sub>O<sub>4</sub> at different magnification.**

### 3.3. FTIR study

The FTIR spectrum of synthesized MgFe<sub>2</sub>O<sub>4</sub> in the range 4000–400 cm<sup>-1</sup> is shown in Fig. 4 (a). It is observed from the spectrum that there are important signatures of absorption bands. FT-IR spectra (Figure 3 a-b) of MgFe<sub>2</sub>O<sub>4</sub> at 800C showed two absorption bands below 600 cm<sup>-1</sup>, a common feature of all spinel ferrites. The high-frequency band ( $\nu_1$ ) lies in the 550 – 600 cm<sup>-1</sup> range and the low-frequency band ( $\nu_2$ ) in the 400 – 440 cm<sup>-1</sup> range. This difference in the band position is attributed to the vibration of tetrahedral and octahedral components in the spinel ferrites [18,19,27]. The inset shows two persistent absorption bands corresponding to the vibration of tetrahedral and octahedral complexes at  $\nu_1$  561 cm<sup>-1</sup> and  $\nu_2$  437 cm<sup>-1</sup>, respectively, which is indicative of formation of spinel ferrite structure [20]. Owing to the high temperature generated during combustion process all the carboxyl, hydroxyl and nitrate groups get eliminated totally. The presence of long shoulder for the A-site is indicative of the presence of other ionic states in that site (i.e. Mg<sup>2+</sup> ions in the A-site). Hence our proposed cation distribution is justified using the FTIR spectrum. It is seen from FTIR data that the normal mode of vibration of tetrahedral cluster (561 cm<sup>-1</sup>) is higher than that of octahedral cluster (437 cm<sup>-1</sup>). This can be due to the shorter bond length of tetrahedral cluster than the octahedral cluster. Waldron has observed the values of  $\nu_1$  and  $\nu_2$  as 565 and 406 cm<sup>-1</sup> for bulk particles of MgFe<sub>2</sub>O<sub>4</sub>. It is worthy to note that there is a decrease in the value of  $\nu_1$ , whereas there is a notable increase in the value of  $\nu_2$  of the present nano-MgFe<sub>2</sub>O<sub>4</sub> when compared with its bulk counterpart. This is due to redistribution or inversion of cations among A and B-site when the material is prepared as nanoparticles. It is seen from our proposed cation distribution that Mg<sup>2+</sup> ions of larger ionic radii replaces Fe<sup>3+</sup> ions of comparatively smaller radii in the A-site. Eventually the change in bond lengths of the ions occupying the sites has resulted in the change in vibrational frequencies.



(a)



(b)

Fig – 3. (a) and (b) are the FTIR spectra of the calcined MgFe<sub>2</sub>O<sub>4</sub> powders.

### 3.4 Raman analysis

It is a method to distinguish the vibrational and structural properties of any given material. MgFe<sub>2</sub>O<sub>4</sub> has a cubic spinel structure of type AB<sub>2</sub>O<sub>4</sub> which belongs to Fd-3m space group with eight formula units per cell. Here 42 vibrational modes are possible due to the 14 atoms present in the smallest Bravais cell. The synthesized Mg ferrite sample is plotted in the frequency range 20 to 600 cm<sup>-1</sup> (figure - 5). According to the group theory it is predicted that the following optical phonon distribution: 5T<sub>1u</sub> + A<sub>1g</sub> + E<sub>g</sub> + 3T<sub>2g</sub>; the 5T<sub>1u</sub> modes are IR active [21], [28], while the other five (A<sub>1g</sub> + E<sub>g</sub> + 3T<sub>2g</sub>) are Raman active modes which is occurred due to the motion of O ions and both the A-site and B-site ions [22,23]. It may be noted that, in ferrites, the modes above 600 cm<sup>-1</sup> belong to the motion of the oxygen atoms in tetrahedral AO<sub>4</sub> group which is not shown in this plot and modes below 600 cm<sup>-1</sup> belong to the motion of the oxygen atoms in octahedral BO<sub>6</sub> [24].

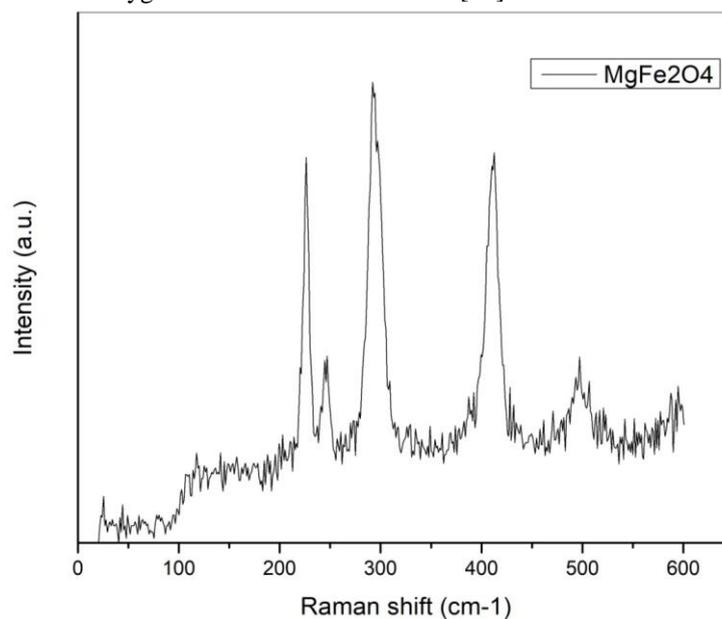


Fig 4 .Raman spectra of pure mg ferrites at room temperature.

### 4. Conclusions

In this work it was observed that nano size grain of metal ferrites can be formed by the solid state reaction of inorganic precursor's method. XRD pattern confirm the phase purity of the synthesized samples and also confirmed that the sample is cubic structure with its lattice parameter 8.376 Å. Raman spectra confirms the five active phonon model for synthesized material which was confirmed by the group theory analysis. Doublet like feature has been observed due to the cation distribution at the both

octahedral and tetrahedral sites. The FESEM image confirms the distribution of grain size is smaller than the other synthesized ceramic route [25,26]. FTIR spectra showed the presence of two absorption bands which is common for all spinel ferrites material.

#### Acknowledgements

Authors are thankful to the Department of Physics, Birla Institute of Technology Meshra and variable energy cyclotron centre Kolkata for facilities.

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