Study on Structural Characterization of Magnesium Nanoferrite

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Abstract

Ferrite materials with tunable electrical and magnetic properties are potential candidates for modern technological applications. The magnesium ferrites; $MgFe_2O_4$ having excellent combination of magnetic and dielectric properties can particularly be used for high-frequency applications. The synthesis conditions such as sintering and composition can manage the properties of these materials. On this background, the magnesium ferrite has been prepared by employing the co-precipitation method. X-ray diffraction (XRD) patterns of prepared samples confirm the formation of a single phase cubic spinel structure. The crystallite size and lattice parameters of the sample have been calculated from XRD data. Functional group of -OH band and Fe-O band have been confirmed from the FTIR study. Scanning Electron Microscopy (SEM) has been employed to observe the morphological features of magnesium ferrite, $MgFe_2O_4$. Response of resistance and capacitance has been studied in the frequency range of 0.3 to 3 MHz and the dielectric constant show the variation at low frequency and both become stable at higher frequency ranges.

Keywards: X-ray diffraction, FTIR, SEM and Microstructure of $MgFe_2O_4$

Introduction

Ferrites include a wide range of materials with various crystal structures, compositions and applications. They are ceramic materials, dark gray or black in appearance and very hard and brittle. Spinel ferrites have interesting magnetic and electrical properties. Nowadays, these materials are largely synthesized in nanometric scale for new and improved properties.

The magnetic and electrical properties of spinel ferrites can be tailored for specific device applications by choosing the cation type and cation distribution between tetrahedral (A) and octahedral (B) sites of the spinel lattice. The preparation conditions, sintering temperature, sintering time and the method of preparation are other important parameters in the synthesis. Magnesium ferrites are suitable materials for miniaturizing the size of antennas, along with enhanced properties. The variations of thermal treatment, type of precursors, molar ratio and synthesis route affect the properties of magnesium ferrite and its area of applications.

Materials and Method

The synthesis route plays an important role on physical, chemical, structural and magnetic properties of spinel ferrites. There are various methods which are applied in bulk ferrite production such as co-precipitation, freeze-drying, gel processing and self-propagating combustion, sonochemical reaction, electro-deposition, microemulsion, citrate precursor method, cold isostatic pressing, hot pressing, tape casting and so on. In this work,

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polycrystalline powders of $MgFe_2O_4$ have been prepared by the chemical co-precipitation route to produce fine particles.

Magnesium nitrate hexahydrate ($Mg(NO_3)_2.6H_2O$), iron nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$) and sodium hydroxide (NaOH) are used as raw materials. Aqueous solutions of analytical graded $Mg(NO_3)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$ have been mixed by magnetic stirring. To obtain smaller size, narrow size distribution and chemically homogeneous ferrite particles, the precipitating reagent (NaOH) has been mixed quickly into the metal solutions. The pH of the solution is maintained at 12.5. For the transformation of metal hydroxides into ferrites, the temperature of the solution has been maintained at 80°C for 40 minutes with constant stirring. Then the solution has been filtered with filter paper and repeatedly washed with distilled water. The washed powder was dried in an electric oven at 100°C for 3 hours to remove water content. The dried powder has been grinded with A-gate motar and calcined at 900°C for 3 hours. After calcination, the phase identification has been conducted by the RIGAKU MULTIFLEX X-ray diffractometer.

The starting materials which are used in the co-precipitation synthesis.The molecular vibrations have been examined by Fourier Transform Infrared Spectroscopy (FTIR). After the samples have been synthesized, the morphological features of the samples have been studied by Scanning Electron Microscope (SEM). The grain size, shape and homogeneity of the samples have been estimated from the SEM images. And then, the sample is made into pellets and final- sintered at 1000°C for 3 hours. After sintering, the phase identification has been conducted by the RIGAKU MULTIFLEX X-ray diffractometer and the morphological features of the samples have been studied by Scanning Electron Microscope (SEM). The density and porosity of the pellects are calculated. Response of resistance and capacitance has been studied at room temperature in the frequency range of 0.3 to 3 MHz.

Results and Discussions

The structural and magnetic properties of the ferrites spinels are sensitive to the details of the preparation methods. Therefore, it is important to characterize the raw material before preparation.

Phase Identification by XRD Technique

In this work, the purity of the raw materials has been checked by XRD technique prior to the preparation of Magnesium ferrite, $MgFe_2O_4$, by co-precipitation method. The X-ray diffraction (XRD) patterns of the prepared samples are taken by the RIGAKU MULTIFLEX X-ray diffractometer. The data has been collected in a 2θ range from 10°C to 70°C. The structural characteristics of the sample are analyzed by XRD method.

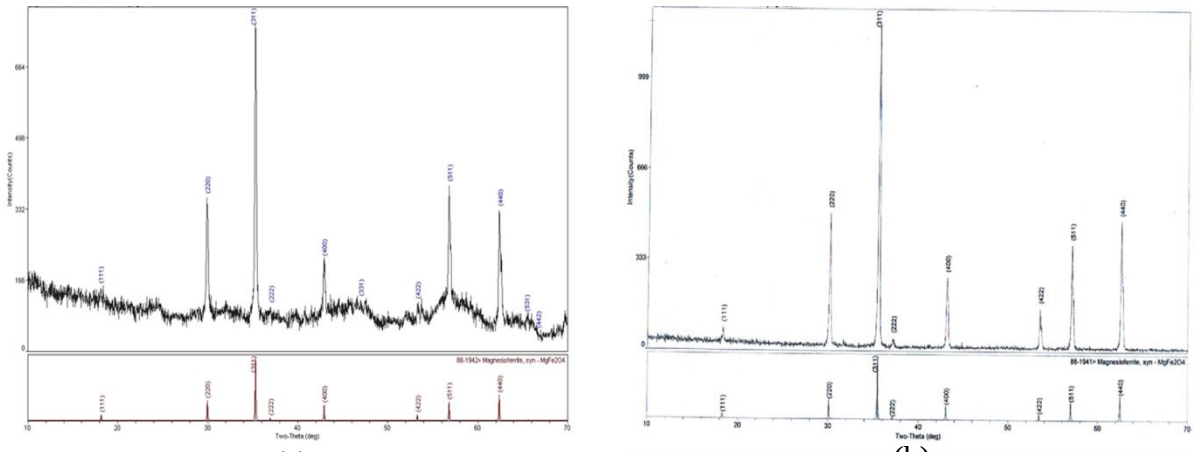
The lattice parameter and crystallite size of the polycrystalline material is calculated from XRD data by using Scherrer's formula.

$$D = \frac{k\lambda}{B\cos\theta} \quad (\kappa = 0.9) \qquad (1)$$

where, "D" is the crystallite size (nm), "λ" is the wavelength of incident X-ray (Å), "θ" is the diffraction angle of the peak under consideration at FWHM (deg) and "B" is the Full Width at Half Maximum (radians).

The diffraction peaks in the XRD pattern show the formation of single phase cubic spinel. All the diffraction peaks exhibit the formation of spinel ferrite. Therefore, it is confirmed that a single phase cubic spinel of $MgFe_2O_4$ has been formed by using co-precipitation method. The crystallite size has been obtained by using Scherrer's formula and is

tabulated in Table 1 and Table 2. It is investigated that the crystallite size has increased with the increase in sintering temperature. The average lattice parameter value of 8.4027 Å and 8.3853 Å which are closed to the typical value of spinel structure confirmed the consistency of synthesis route in this work. After final sintering, the average crystallite size is about 41.96 nm.



(a) (b)

Figure 1. XRD spectrum of $MgFe_2O_4$ (a) pre-sintered at 900ºC and final- sintered at 1000ºC

Table 1. XRD data of $MgFe_2O_4$ pre-sintered at 900ºC

No	2θ (deg)	Diffraction Peak (hkl)	FWHM (deg)	B (rad)	Lattice Constant a (Å)	Crystallite size (nm)
1	30.06	(220)	0.256	0.0045	8.4018	32.13
2	35.38	(311)	0.232	0.0041	8.4067	35.94
3	43.02	(400)	0.288	0.0050	8.4032	29.65
4	53.344	(422)	0.332	0.0058	8.4067	26.77
5	62.50	(440)	0.296	0.0052	8.3993	31.39
6	56.92	(511)	0.275	0.0048	8.3985	32.86
Average			0.279	0.0049	8.4027	31.46

Table 2. XRD data of $MgFe_2O_4$ final-sintered at 1000ºC

No	2θ (deg)	Diffraction Peak (hkl)	FWHM (deg)	B(rad)	Lattice Constant a(Å)	Crystallite size(nm)
1	30.141	(220)	0.183	0.0032	8.3792	44.95
2	35.488	(311)	0.200	0.0035	8.3828	41.69
3	43.132	(400)	0.213	0.0037	8.3824	40.09
4	53.480	(422)	0.222	0.0039	8.3871	40.07
5	62.612	(440)	0.222	0.00387	8.3857	41.89
6	57.026	(511)	0.210	0.0036	8.3845	43.05
Averae			0.208	0.0036	8.3853	41.96

Porosity and Density Measurement

The porosity (P) of the sample has been determined by using the formula

$$P=1-\frac{d_m}{d_x} \qquad (2)$$

where d_m and d_x are the measured density and the theoretical density, respectively.

The measured density has been calculated using the relation

$$d_m=\frac{m}{\pi r^2 h}, \qquad (3)$$

where h is the height, r the radius and m the mass of the cylindrical pellet of the sample.

The theoretical density has been calculated by using the formula,

$$d_x=\frac{8M}{NV} \qquad (4)$$

In the spinel structure, 8 is the number of formula units in a unit cell. N is the Avogadro's number, M is the molecular weight of the one formula unit and V is the volume of the unit cell.

The complex relative permittivity of the prepared samples has been measured in the frequency range of 300 Hz to 3 MHz using a precision component analyzer by the capacitance method. The dielectric constant (ε_r) was calculated by the relation.

$$\varepsilon_r=\frac{Cd}{\varepsilon_0 A}, \qquad (5)$$

where d the thickness, C is the capacitance, ε_0 is the permittivity of free space and A is the cross-sectional area of the pellet. The dielectric constant of samples has been determined from experimentally obtained capacitance values. The dielectric properties of ferrites are dependent upon several factors such as method of preparation, chemical composition, grain structure and grain size.

Molecular Vibration

The molecular vibrations have been examined by Fourier Transform Infrared Spectroscopy (FTIR). The strength of IR peak is roughly dependent on the change in dipole moment during vibration. The FTIR spectra of $MgFe_2O_4$ powder with different calcination temperatures are presented in Figure 3. The vibrational frequencies of the chemical bonds in the $MgFe_2O_4$ nanoparticles can be assigned from FTIR spectra which were recorded in the region 400 cm^{-1} to 4000 cm^{-1}. According to the FTIR spectra, the characteristic stretching vibrations of (Fe-O) in the calcined sample are found to be at 574.81 cm^{-1} for 1000ºC. This vibration is an indicative of formation of spinel ferrite structure. Therefore, it can be said that FTIR analysis strongly supports the XRD result.

Microstructure of $MgFe_2O_4$

The microstructure and morphology play the important roles in determining magnetic and electric transport properties. These studies for the materials are essential in order to understand the relationship between their processing parameters as well as the behavior when they are used in practical applications. Microstructures of the sintered $MgFe_2O_4$ have been analyzed by a high resolution scanning electron microscope (SEM). The SEM images of $MgFe_2O_4$ final-sintered at different temperatures are given in Figure 4 (a), (b), (c) and (d). The variation of average grain size with the calcination temperature is shown in Table 3. As seen in SEM images, the grains are agglomerated in irregular shape for all heat-treatments. With the increasing temperature, the average grain size decreases from 1.75μm to 1.19 μm. The calculated density is 2.46 gcm-^{3}and the porosity is 0.46.

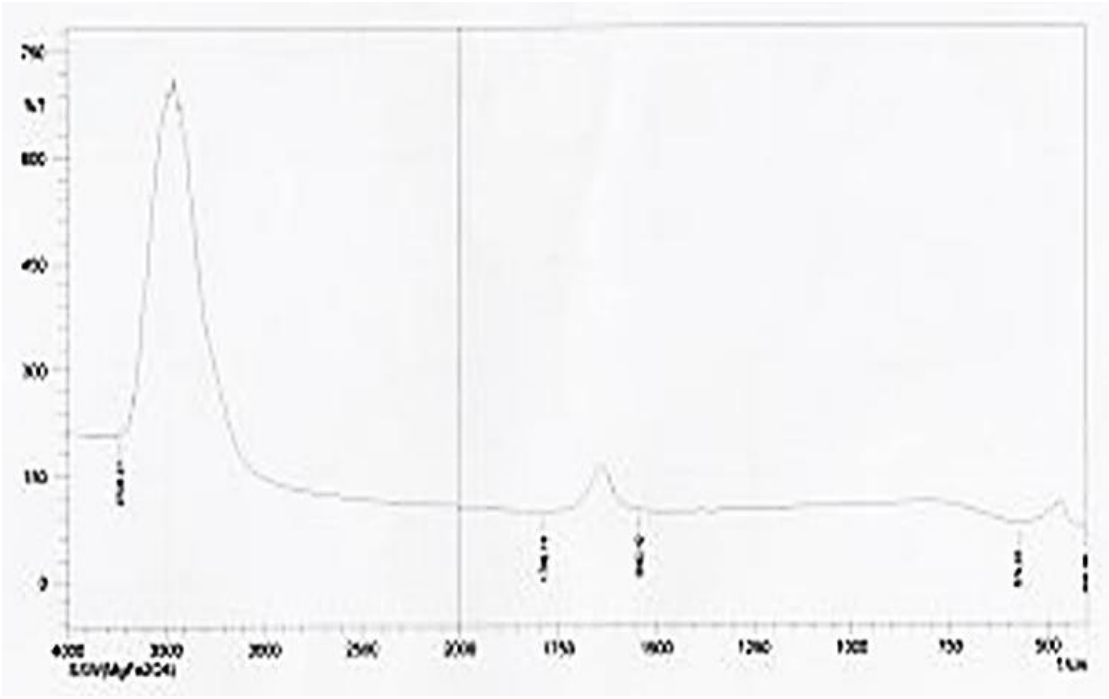


Figure 3. The FTIR spectrum of $MgFe_{2O4}$ sintered at 1000ºC

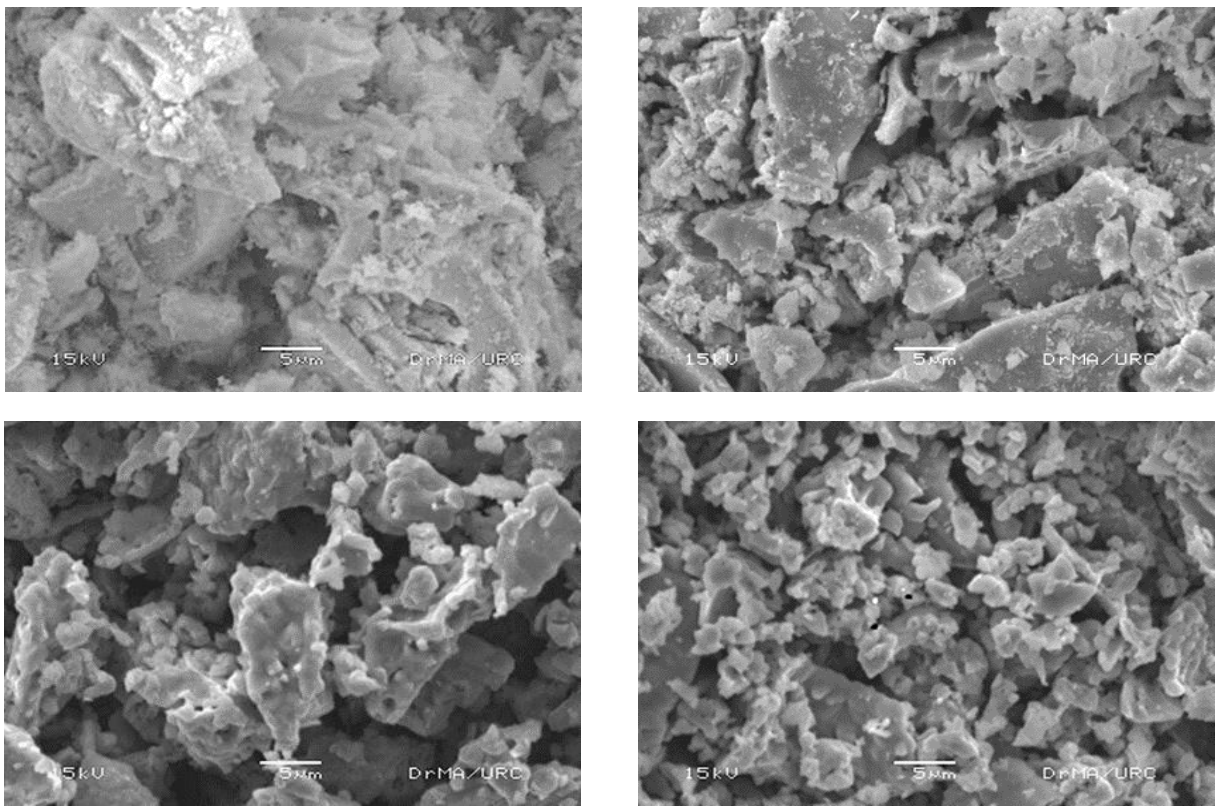


Figure 4. SEM micrographs of MgFe2O4 final-centered at (a)700ºC, (b) 800ºC, (c) 900ºC and (d) 1000ºC

Table 3. Variation of Average Grain Size with sintering temperatures

No	Final-sintering temperature(°C)	Average grain size (μm)
1	700	1.75
2	800	1.59
3	900	1.49
4	1000	1.19
Average		1.51

Frequency Dependent Dielectric Constant

The variations of dielectric constant with frequency are shown in Figures 8. From these graphs, the values of dielectric constant of the samples show a variation in lower frequency region. The variation of dielectric constant in lower frequency region is due to the grain boundary defects of ferrite and the dielectric constant becomes stable in higher frequency region. In the lower Frequency region, the dipole polarization is hindered by the grain boundaries; however, this effect can be overcome in the higher frequency region.

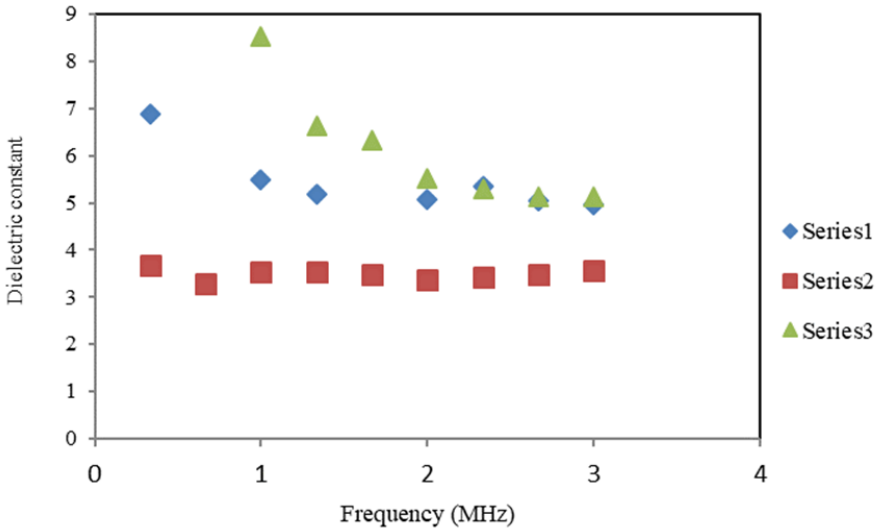


Figure 8. The variations of dielectric constant with frequency

Conclusion

Magnesium Ferrite, $MgFe_2O_4$, has been successfully prepared by co-precipitation method in this work. As the starting powder characteristics are strongly determined the product, the raw materials have been selected to ensure their purities. The XRD characterization of the sintered ferrite has been identified the formation of the typical cubic spinel structure. It has also been confirmed that the spinel phase is stable until 1000°C. The lattice parameters and crystallite size have been calculated for further characterization. The sizes of crystallites in the sample have been evaluated by using the FWHM of the most intense peaks and the results confirm the formation of ferrite particles. The average crystallite size of $MgFe_2O_4$ decreased until nanometer range due to the synthesis by chemical co-precipitation technique. The typical lattice parameter value of 8.4027 Å and 8.3853Å has confirmed the consistency of synthesis route in this work. Based on the SEM micrographs, when the samples

have been sintered at higher temperature, subsequent grain growth has taken place. The FTIR study also confirmed the presence of functional groups in $MgFe_2O_4$ nanoparticles. At the final-sintering temperature, the average grain size also increases to 1.75 μm. The density is found to be 2.46 gcm^{-3} and the porosity is 0.46. The values of dielectric constant of the samples show a variation in lower frequency region due to the grain boundary defects of ferrite and the dielectric constant becomes stable in higher frequency region.

The frequency dependent electrical properties, temperature dependent electrical properties and magnetic properties of $MgFe_2O_4$ will be investigated in the future. The behavior of these properties will be linked with the results obtained by XRD, FTIR and SEM analysis.

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References

Khu Rmi R.S. (2005). “Material Science” S. Chand Company.

Pradeep A et al (2008). “Production of single phase nano size $NiFe_2O_4$ particles using sol–gel auto combustion route by optimizing the preparation conditions” Mater. Chem. Phys.,112.

Sayed M.M. EI (2005). “Rare-earth substitution effect on the quality of Mg-Ti “ferrite” Ani Shams University, Roxy, Cairo, Egypt.

Vijaya Kumar K, Ravinder D (2001). “Electrical transport properties of erbium substituted Ni-Zn ferrites”, Osmania University, Hyderabad- 500 007, A.P., India.

Yang Leng, (2008). ‘Material Characterization” Introduction to Microscopic and Spectroscopic Methods Second Edition. Ahmad M. A, Kasha M. O, Sayed M.M. EI (2005) “Enhancement of the physical properties of rare-earth-substituted Mn-Zn ferrites prepared by flash method, Ani Shams University, Cairo, Egypt.