Effect of calcination temperature on structural, dielectric and magnetic properties of $Mg_{0.6}Zn_{0.4}Fe_2O_4$ ferrite nanoparticles.

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***Abstract*— The sample $Mg_{0.6}Zn_{0.4}Fe_2O_4$ was prepared by a sol-gel auto-combustion method. The obtained sample was calcinated at 400⁰C, 500⁰C & 600⁰C temperatures. Then, the samples were characterized by powder X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis, dielectric and magnetic properties. XRD results confirm the formation of a cubic spinel-type structure with an average crystallite size increased with Calcination temperature from 32.17 to 34.73 nm. Lattice parameter decreases with increasing calcination temperature, due to the small ionic radius of the Mg^{2+} ion. The SEM images show the morphology of the samples as spherical shaped particles in agglomeration. The dielectric constant and saturation magnetization values increased with increasing calcination temperature.**

***Keywords*— XRD, SEM, LCR, VSM and Solgel auto combustion method**

I. INTRODUCTION

Ferrites form a very good class of electrical materials because of their high resistivity and low loss behaviour, and hence have vast technological applications over a wide range of frequencies. Ferrites are preferred in the field of electronics and telecommunication industry because of their novel electrical properties which makes them useful in radio-frequency circuits, high-quality filters, rod antennas, transformer cores, read/write heads for high digital tapes and other devices. Hence it is important to study their dielectric behaviour at different frequencies. The dielectric properties of ferrites are dependent on several factors, such as the method of preparation, heat treatment, sintering conditions, chemical composition, cation distribution and crystallite size [1].

Ferrites, a distinct class of magnetic materials known as ferromagnetic have spinel structure. They consist of spontaneously magnetized domains and show the phenomena of magnetic saturation and hysteresis. Spinel ferrites possess properties of both magnetic materials and insulators and are important in many technological applications. The interesting physical and magnetic properties of spinel ferrites arise from the ability of these compounds to distribute the cations among the available tetrahedral (A) and octahedral (B) sites [2].

Spinel ferrites have gained a lot of attention because of their remarkably high electrical and magnetic flux induction. They are considered a good dielectric and are found in many technological applications. Increased application of ferrites has led to the development of many chemical methods which includes hydrothermal, co-precipitation and sol-gel for the preparation of stoichiometric and chemically pure spinel ferrites [3].

Among the mixed Zn ferrites, Mg–Zn ferrite is a promising candidate for a wide range of applications [4,5]. Parameters such as the magnetization, coercivity and permittivity of Mg-Zn ferrites strongly depend on particle size, which depends in turn on calcination time and temperature. The major controllable factor responsible for grain size and microstructure of the materials is the mode of preparation [6]. Generally, ferrites are prepared by ceramic methods that have limited ability to produce nanoscale particles [7]. Most chemical methods also require long processing time, expensive chemicals and a special experimental arrangement. In contrast, a solution combustion (SC) method used to prepare nanocrystalline ferrites is a useful and attractive technique. This method has the benefit of producing an exothermic, fast and self-sustained chemical reaction. The reactants in this method are mixed at the atomic scale, which reduces both the synthesis temperature and time. Additionally, combustion synthesis only requires relatively simple equipment to produce ultrafine and homogeneous products [8,9]. As a continuation of our previous work [10], we report and discuss herein the effect of calcination both on particle size and on the magnetic properties of Mg0.6 Zn0.4 Fe2O4.

II. EXPERIMENTAL

Commercially available metal nitrates of magnesium nitrate ($Mg(NO_3)_2.6H_2O$), zinc nitrate ($Zn(NO_3)_2.6H_2O$) and ferric nitrate ($Fe(NO_3)_2.9H_2O$) (all are AR grade Sigma Aldrich, USA, 99.9% purity), citric acid were used as starting materials and ammonia is used as fuel material for this reaction. The appropriate metal nitrates and fuel was taken in a silica glass beaker containing volume 500 ml placed on the stirrer under constant temperature 200⁰C. The solution boils, froths, catches fire and burns with a smouldering flame to produce a voluminous and porous brown coloured nanocrystalline product accompanied by the release of a large amount of gas. The detailed procedure is provided in our earlier report [10]. The obtained product was then calcined at 400⁰C, 500⁰C and 600⁰C for four hours in an ambient atmosphere.

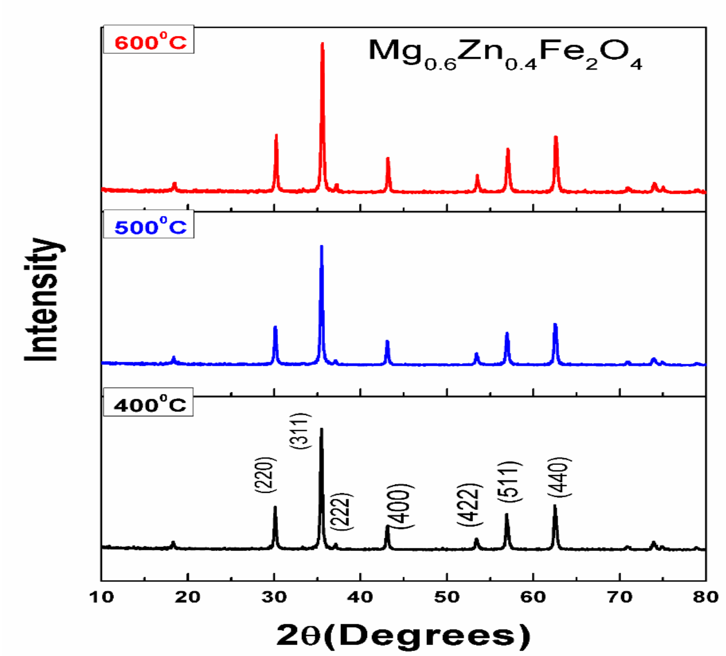
III. RESULTS AND DISCUSSION

A. XRD Analysis

Fig(1) shows XRD patterns of Mg0.6Zn0.4Fe2O4 calcination at 4000C, 5000C and 6000C. All the samples show the formation of the cubic spinel-type structure of (JCPDS card no 22-1012) with an average crystal size in the range of 32.17 – 34.73 nm[11]. All the samples show the presence of (220),(311), (400), (422), (511) and (440) diffraction peaks in the scanning range 10° to 80°. No other phases are detected in the Mg-doped ZnFe2O4 samples, which indicate that all the samples exhibit the single-phase cubic spinal structure. The average crystallite size of the samples is calculated from the diffraction peaks at (311), (440), and (511) planes in the XRD profile, in accordance with Debye–Scherrer formula [12].

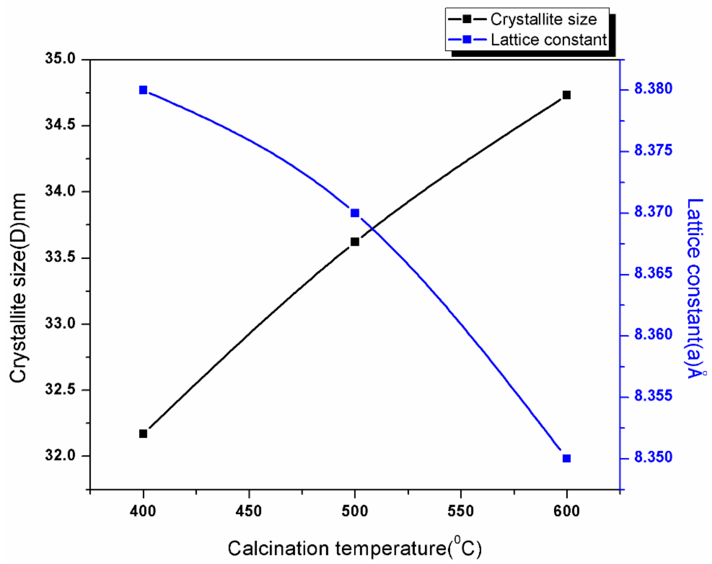
$$D=0.9\lambda/\beta COS\Theta \qquad (1)$$

Where D is the crystallite size, λ is the wavelength, β is FWHM (the full width at half maxima), and θ is the Bragg's angle.



Fig(1) XRD patterns of 0.6 M % Mg-doped ZnFe2O4 sample calcinated at 400°C, 500°C and 600°C

Fig (2) shows the variation of crystallite size and Lattice constant with respect to calcination temperature. It has been observed that crystallite size(D) varies from 32.17 to 34.73 nm with increasing calcination temperature. Unlike lattice constant is varies from 8.38 to 8.35nm. This is mainly due to that small ionic radius of Mg ions (0.67Å) replacing the larger size of Zn ions (0.74Å) with the increase of temperature[13].



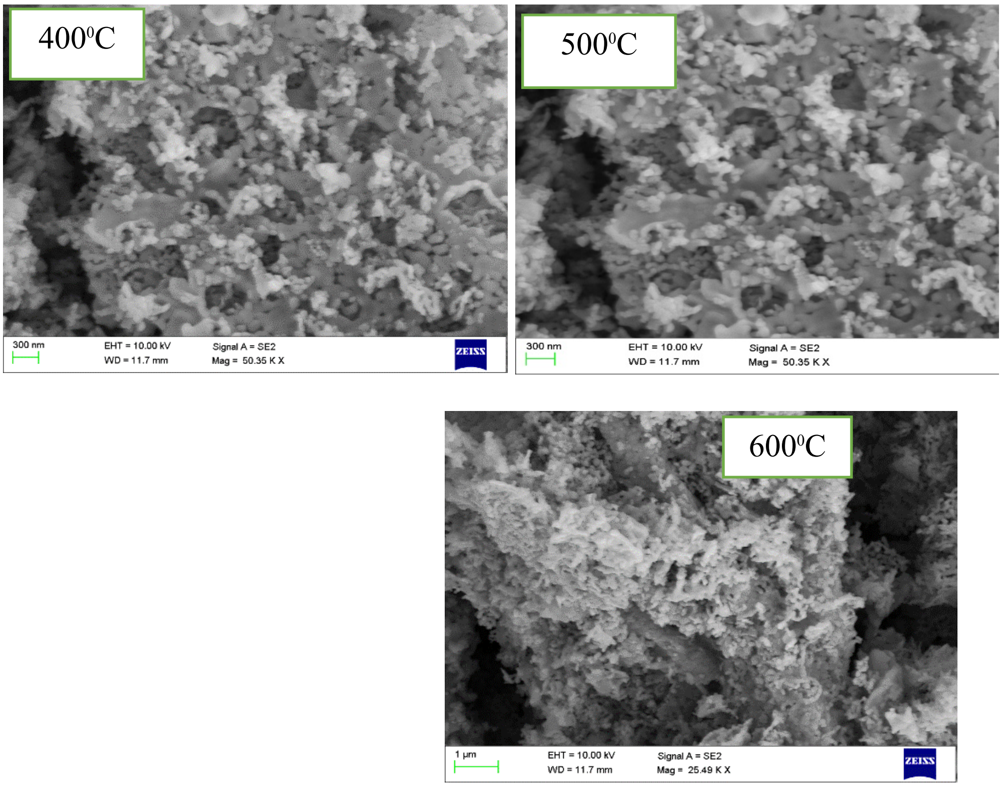
Fig(2) Variation of Crystallite size and lattice constant of $Mg_{0.6}Zn_{0.4}Fe_2O_4$ sample at 400°C, 500°C and 600°C

Table I The observed structural parameters of $Mg_{0.6}Zn_{0.4}Fe_2O_4$ nano ferrites at 400^{0}C, 500^{0}C and 600^{0}C

COMPOSITION (X)	CALCINATION TEMPERATURE (^{0}C)	CRYSTALLITE SIZE (D) nm	LATTICE CONSTANT(a) Å
$Mg_{0.6}Zn_{0.4}Fe_2O_4$	400	32.17	8.38
	500	33.62	8.37
	600	34.73	8.35

B.SEM Analysis

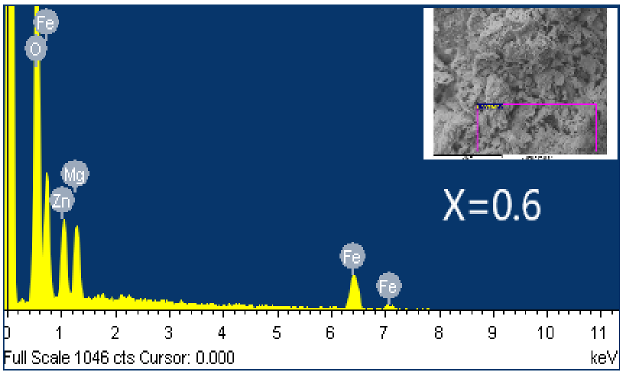
The SEM images of the Mg0.6Zn0.4Fe2O4-ferrite samples (Fig.3) show that the morphology of particles was almost spherical, regular in shape and dispersed uniformly, but agglomerated to some extent due to the interaction between the magnetic nanoparticles, whereas the gel exhibits a relatively porous network. The pressure exercised by gaseous species should be responsible for the breakup of the porous structure. Heat treatment resulted in an agglomeration of the powder as a function of the calcining temperature which is typical for the spinel ferrites. Therefore, some degree of agglomeration at the higher calcination temperature appears unavoidable. In many cases of nanocrystalline ferrites, it is observed that there is a tendency of agglomeration among the nanoparticles [14].



Fig(3) SEM images of $Mg_{0.6}Zn_{0.4}Fe_2O_4$ ferrite sample at 400^{0}C,500^{0}C and 600^{0}C

C. EDS analysis

The EDS analysis was performed to identify the elemental compositions in $Mg_{0.6}Zn_{0.4}Fe_2O_4$ nano ferrite samples, as shown in Fig(4) and their elemental and atomic percentages are mentioned in Table (2). All the images show the existence of elements used for the synthesis like Mg, Zn, Fe, and oxygen atoms. Except for these elements, no other impurity elements present in the samples. Therefore the prepared samples are defect-free and homogenous.



Fig(4) EDS image of $Mg_{0.6}Zn_{0.4}Fe_2O_4$ ferrite sample

Table II. The elemental and atomic percentages of $Mg_{0.6}Zn_{0.4}Fe_2O_4$

ELEMENT	O		Mg		Zn		Fe	
(x)	Element %	Atomic %	Element %	Atomic %	Element %	Atomic %	Element %	Atomic %
$Mg_{0.6}Zn_{0.4}Fe_2O_4$	29.12	57.13	5.59	7.21	12.65	6.08	52.64	29.58

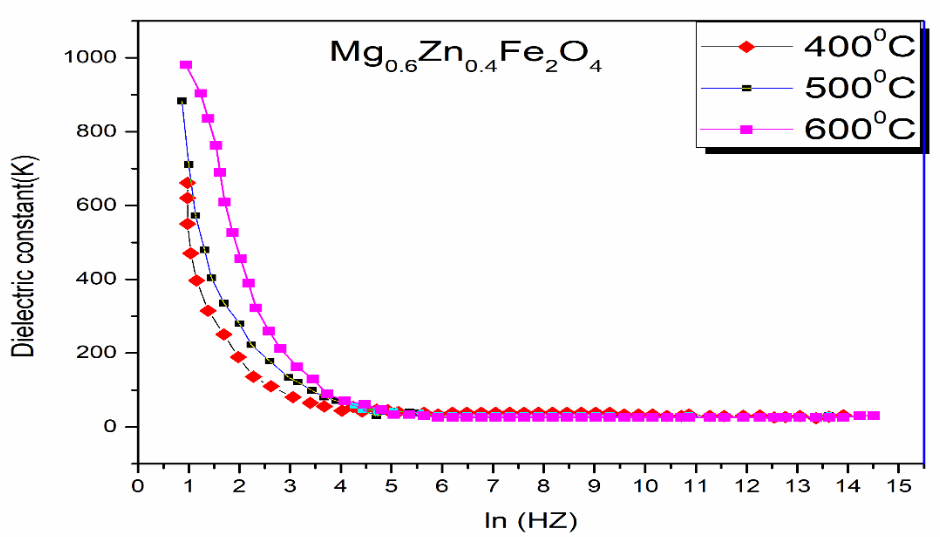
D. Dielectric properties

(i)Effect of frequency on dielectric constant:

The frequency-dependent dielectric constant of $Mg_{0.6}Zn_{0.4}Fe_2O_4$-ferrites are calcined at 400°C,500°C and 600°C is shown in Figure (5). The dielectric constant decreased with an increase in frequency and it follows the Koops phonological theory [15]. According to Koops theory, the dielectric constant decrease with an increase in frequency is attributed to the decrease of polarization. Ultimately, it reaches a constant value because beyond a certain critical value of frequency of external field the electronic exchange between ferrous and ferric ions cannot follow the alternating field.

(ii)Effect of temperature on dielectric constant:

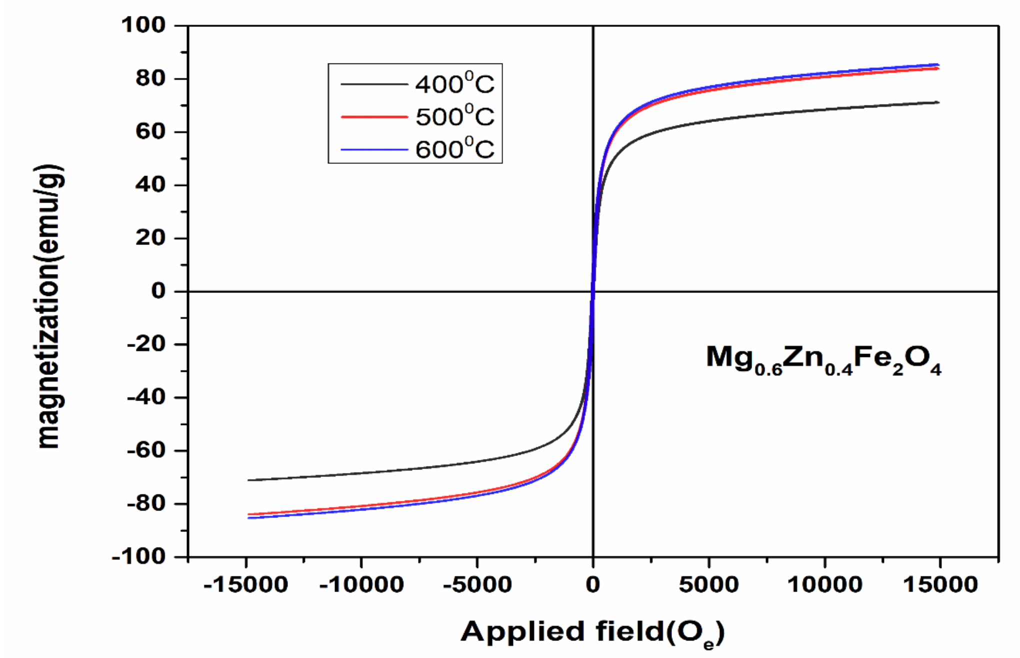
The natural behaviour of almost all ferrites, the dielectric constant(k) of material decreases with increasing the frequency. At low frequencies the value of the dielectric constant is high. At lower frequencies, the enrichment in the dielectric constant with temperature is more pronounced than at higher frequencies. The K of any material, in common, is due to electronic, ionic, dipolar, and interfacial polarization. Interfacial and dipolar polarization are played a crucial role at low frequencies and are strongly dependent on temperature. The creation of lattice defects and dipolar polarization is due to the change in temperature of the interfacial polarization. The effect of temperature is highly pronounced on the interfacial polarization than that of the dipolar polarization which results in the rapid increase of dielectric constant with the increase of temperature at low frequencies [16].



Fig(5) Variation of Dielectric constant of $Mg_{0.6}Zn_{0.4}Fe_2O_4$ with Applied frequency

E. Magnetic properties

The fig (6) shows M-H curve for $Mg_{0.6}Zn_{0.4}Fe_2O_4$-ferrite nanoparticles are calcined at 400°C, 500°C and 600°C. Here both $Mg^{2+}$and Zn^{2+} are nonmagnetic ions.so only Fe^{2+} ions are contributed net magnetic moment. The sample corresponding to the lower calcination temperature (400 °C) had a saturation magnetization (M_s) value of 65.58 emu/g. The samples corresponding to higher calcination temperatures of 500 °C and 600°C had M_s values of 84.59 emus/g and 85.30 emu/g, respectively. The increase of the M_s with the increase of the calcination temperature can be attributed to the cations redistribution that expected at the previous discussion where the Fe^{3+} ions indicate migrate to octahedral sites with the increase of calcination temperature. It should be noted that the magnetic moment of Fe^{3+} ions is greater than that of both Mg^{2+} and Zn^{2+} ions. So that the dominant redistribution of Fe^{3+} ions at octahedral sites will increase the total number of the magnetic moment which appears as the increase of the saturated magnetization in the $Mg_{0.6}Zn_{0.4}Fe_2O_4$ ferrite nanoparticles[17].



Fig(6) Variation of Saturation Magnetization of Mg0.6Zn0.4Fe2O4 with Applied field at 400°C, 500°C and 600°C

IV CONCLUSIONS

The sample is prepared using sol-gel auto combustion method and calcined at 400°C,500°C and 600°C. From XRD pattern confirmed the formation of the spinel structure. The crystallite size increased from 32.17 to 34.73 nm. From SEM micrographs all samples are shown well agglomerated and spherical shape. The effect of calcination temperature on dielectric constant values is varied from 650 to 1000. Similarly, the saturation magnetism values are increased from 65(emu/g) to 84 (emu/g) with increasing calcination temperature. Finally, it has been observed that both magnetic and dielectric properties depend on crystallite size.

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