Structural, electrical, and magnetic properties of Zn substituted magnesium ferrite

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ABSTRACT

Zinc substituted magnesium (Mg-Zn) ferrites with the general formula Mg_{1-x}Zn_xFe_2O_4 (x = 0.00, 0.25, 0.50, 0.75, and 1.00) were prepared using the solution combustion route. The dried powder after calcination (700°C for 2 h) was compacted and sintered at 1050°C for 3 h. The structural, morphological, dielectric and magnetic properties of the sintered ferrites were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), impedance spectroscopy, and vibration sample magnetometry (VSM). The XRD analysis of sintered samples confirmed that the expected spinel cubic phase was formed for all samples. The crystallite sizes evaluated using Scherrer’s formula were found to be in the range of 47–80 nm. SEM analysis showed homogeneous grains with a polyhedral structure. The electrical conductivity increased with increasing frequency, which is normal dielectric behaviour for such materials. The dielectric constant, dielectric loss tangent, and AC conductivity were found to be lowest for x = 0.50. The VSM results showed that the zinc concentration had a significant influence on the saturation magnetization and coercivity.

Key words: D: Ferrites: C: Dielectric properties: C: Magnetic properties.

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1. Introduction

In recent years, there has been growing interest from the magnetic, electronic, and microwave fields for developing spinel ferrite materials with improved electromagnetic properties at higher frequencies. Ferrites are considered superior to other magnetic materials for use at higher frequencies, because of their low dielectric losses and high electrical resistivity [1]. Spinel ferrites are technologically important materials and have potential applications, including high-density magnetic storage, electronic and microwave devices, gas sensors, and magnetically guided drug delivery [2].

Mixed zinc ferrites are technologically interesting materials with applications ranging from magnetic storage devices to catalytic water splitting [3]. Mg-Zn ferrites are used in power transformers, microwave devices, and telecommunications due to their high permeability and electrical resistivity [4]. The structural, magnetic, electrical, and dielectric properties of ferrites depend on the method of preparation, chemical composition, sintering time, sintering temperature, and level of doping [5]. Ferrite nanoparticles are generally prepared by physical and chemical methods, such as ceramic processing, co-precipitation, hydrothermal methods, and via the fabrication of reverse, or, normal micelles [4,6,7]. For the past two decades, the solution combustion method has attracted a great deal of attention for synthesizing oxides with well controlled compositions. The solution combustion method is a popular method because it provides a fast, self-sustaining, and exothermic chemical reaction between metal salts and a suitable organic fuel. In this technique, most of the heat required for synthesis is supplied by the reaction itself [8-10]. This study focuses on the synthesis and electromagnetic properties of Zn$^{2+}$ substituted magnesium ferrites prepared by the solution combustion method using urea and sugar as the fuel.
2. Material and methods

Various Mg-Zn ferrites were prepared with different levels of Zn substitution using the solution combustion method. A stoichiometric mixture of AR grade ferric nitrate (Fe(NO\textsubscript{3})\textsubscript{3}.9H\textsubscript{2}O), magnesium nitrate (Mg(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O), zinc nitrate (Zn(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O) 99.9% pure MERK) and the sugar and urea fuel mixture was used: the detailed synthesis procedure is reported elsewhere [11]. A dark brown powder was obtained and then calcined at 700°C for 2 h at a heating rate of 10°C/min. This calcination step is necessary to improve the crystallization and homogeneity of the cation distribution in the spinel. A fixed amount of calcined powder was mixed with a few drops of 3 wt.% aqueous polyvinyl alcohol (PVA) as a binder and compacted at a pressure of 75 kg/cm\textsuperscript{2} for 5 min to form pellets with a diameter of 13 mm and a thickness of 2 mm. These pellets were sintered at 1050°C in air for 3 h and then the furnace was allowed to cool to room temperature. Silver paste was painted on both sides of the pellets to prepare parallel plate capacitor geometry with the ferrite material. The pellets were dried in a hot air oven (50°C) before the characterization measurements to avoid the effect of humidity.

The phase purity of the sintered ferrite pellets was studied using a PANalytical X’pertPRO X-ray diffractometer with Cu–K\textalpha radiation (\(\lambda = 1.5406 \text{ Å}\)). Scanning was performed from 20° to 70° with a step size of 2 °/min. The lattice constant, crystallite size and X-ray density were determined from the XRD data. The morphological characteristics of fractured surfaces of the samples were studied using scanning electron microscopy (SEM, JEOL-JSM Japan). The elemental composition of the samples was calculated using energy dispersive X-ray spectroscopy (EDS). The number of moles of each element present in the composition \(\text{Mg}_{1-x}\text{Zn}_{x}\text{Fe}_2\text{O}_4\) was calculated using the observed wt.% of each element from EDS data as follows:

\[
\text{No. of moles of Me} = \frac{\text{Observed wt}\% \text{ of Me from EDS}}{\text{Molecular wt of sample} \times \text{Atomic wt of Me} \times 100}
\]  

(1)
An Alpha-A high performance frequency analyzer (NOVACONTROL GmbH) was used to carry out the dielectric measurements at room temperature in the frequency range of $10^2$ Hz to $10^7$ Hz. The dielectric constant ($\varepsilon'$) was calculated using the following relationship:

$$\varepsilon' = C_p t / \varepsilon_o A$$ (2)

where the permittivity of free space $\varepsilon_o = 8.854 \times 10^{12} \text{ F/m}$, $t$ is thickness of the pellet, $A$ is the cross sectional area of the pellet and $C_p$ is the capacitance of the pellet.

The loss tangent ($\tan \delta$) was obtained using the following relationship:

$$\tan \delta = \frac{1}{2\pi f R_p C_p}$$ (3)

where $R_p$ is the resistance of the pellet. The AC conductivity was calculated using the following formula:

$$\sigma_{ac} = \frac{2\pi f \varepsilon \varepsilon_o \tan \delta}{\varepsilon'}$$ (4)

where $f$ is frequency.

The magnetic properties of the samples were measured using a vibrating sample magnetometer (VSM, Model Lakeshore 7410) using applied magnetic fields of $\pm$ 15 kOe at room temperature. The saturation magnetization ($M_s$) and coercivity ($H_c$) were determined from the obtained hysteresis loops.

3. Results and discussion

3.1 XRD analysis

Fig. 1 shows the X-ray diffraction patterns of Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ ($x = 0.00, 0.25, 0.50, 0.75$ and $1.00$) ferrites sintered at 1050$^\circ$C. The XRD patterns of the sintered samples characteristic were of the cubic spinel structure and no impurity peaks were observed. The lattice parameters were determined by indexing the XRD patterns. The lattice parameter ($a$) of the sintered samples was found to increase with increasing Zn content obeying Vegard's law [12]. This is attributed to the larger ionic radius of Zn$^{2+}$ (0.82 Å) compared with Mg$^{2+}$ (0.66 Å) [6]. The lattice parameters for the samples with different Zn$^{2+}$ contents are shown in
Table 1. A similar trend was reported previously for Mg-Zn ferrites [13-15]. The crystallite size \((D)\) was calculated from the \((311)\) peak using Scherrer’s formula [16]. This peak narrowed with increasing doping, indicating a decrease in the d-spacing (increase in the lattice parameter). The crystallite sizes of the sintered ferrites were in the range of 47 - 80 nm. The X-ray density \(d_x\) was determined using the relationship \(d_x = ZM/N\alpha^3\) [17], where \(M\) is the molecular weight of the sample, \(N\) is Avogadro’s number, and \(Z\) is the number of chemical units per unit cell, (8 for cubic spinel). The bulk density \(d_b\) of the samples was calculated using the formula \(d_b = m/\pi r^2 h\) where, \(m\) is the mass, \(r\) is the radius and \(h\) is the height of the pellet. It can be seen from the data shown in Table 1 that the bulk density increased with increasing \(\text{Zn}^{2+}\) content. The increase in the density is associated with the increased atomic weight resulting from the substitution of \(\text{Mg}^{2+}\) ions with \(\text{Zn}^{2+}\) ions. The atomic weights of \(\text{Zn}^{2+}\) and \(\text{Mg}^{2+}\) are 65.38 and 24.31 amu, respectively. The apparent porosity \((P)\) was calculated from the difference between the bulk and X-ray densities, i.e., \(P = (1 - d_b/d_x).\) From Table 1 it is evident that the calculated porosity increased with \(\text{Zn}^{2+}\) concentration. The larger atomic weight of zinc increases the bulk density, which may be responsible for the increase in porosity.

3.2 Morphology and composition

SEM micrographs of the fracture surfaces of \(\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4\) \((x = 0.00, 0.25, 0.50, 0.75\) and 1.00\) samples are shown in Fig. 2 along with particle size distribution histograms. The samples showed well defined grains and grain boundaries consisting of combinations of small and large grains with few pores. The grain size derived from the SEM micrographs was larger than the crystal size calculated from the XRD data (Table 1). This indicates that every grain is an aggregate of a large number of crystallites.
EDS spectra (Fig. 3) indicate the presence of Mg, Fe, Zn and O in all samples and the calculated quantitative data from the EDS analysis of all samples are given in Table 2.

3.3 Dielectric properties

The dielectric properties of ferrites are influenced largely by the synthesis method, grain size and cation distribution. The $\varepsilon'$ as a function of frequency for $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.00, 0.25, 0.50, 0.75$ and $1.00$) ferrites is shown in Fig. 4. It is observed that $\varepsilon'$ for all compositions studied here decreased sharply with increasing frequency and then reached a constant value at higher frequencies. This behaviour is considered normal dielectric dispersion in spinel ferrites, which is ascribed to Maxwell-Wagner type polarization in agreement with the Koops phenomenological theory [18-20]. According to this theory, the resistive grain boundary effects dominate those of the grain bulk and result in the observed dispersion. The dispersion in the low frequency region and corresponding high values of $\varepsilon'$ are due to the space charge effect arising from $\text{Fe}^{2+}$ ions, oxygen vacancies, and grain boundary defects. In the high frequency region, the space charge effect is reduced, as the slow moving species are unable to follow the applied field resulting in a decrease of $\varepsilon'$ [21].

In the present study, it was observed that $\varepsilon'$ decreased with the increasing concentration of non magnetic $\text{Zn}^{2+}$ in the $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ compositions. This is due to an increase in the resistivity of magnesium ferrite with the substitution of $\text{Zn}^{2+}$, as the $\varepsilon'$ is directly proportional to the square root of conductivity. A close examination of Fig.1 indicates the maximum $\varepsilon'$ dispersion with frequency for a $\text{Zn}^{2+}$ content of $x = 0.75$, probably due to the formation of $\text{Fe}^{2+}$ in the octahedral sites. The dielectric loss tangent ($\tan\delta$) determines the energy loss from the applied field in the samples at different frequencies. Dielectric loss occurs when the polarization lags behind the applied field: it is caused by impurities and defects in the crystal. The variation of $\tan\delta$ with the frequency is shown in Fig. 5 where it can be seen that the $\tan\delta$ decreases with an increasing frequency for all samples investigated here.
In the low frequency region, which corresponds to high resistivity due to grain boundary effects, more energy is required for electron exchange between Fe$^{2+}$ and Fe$^{3+}$ ions and hence, energy loss (and $\tan\delta$) is high. Conversely, in the high-frequency region, which corresponds to the low resistivity grain bulk, a small amount of energy is needed for electron exchange between Fe$^{2+}$ and Fe$^{3+}$ ions and hence the energy loss (and $\tan\delta$ value) is small. A maximum in dielectric loss versus frequency appears when the frequency of the hopping charge carriers coincides with the frequency of the applied field. The total conductivity of the ferrites is expressed as follows:

$$\sigma (\omega, T) = \sigma_{dc}(T) + \sigma_{ac}(\omega, T)$$  \hspace{1cm} (5)$$

where, $\sigma_{dc}$ is the DC conductivity due to band conduction and is a frequency independent function. The term $\sigma_{ac}$ is the $ac$ conductivity due to the hopping process between octahedral sites and is a frequency dependent function. The pure AC conductivity obeys the power law given by the following relationship [22]:

$$\sigma_{ac} = A(T)\omega^n$$ \hspace{1cm} (6)$$

where, $A(T)$ is the temperature dependent factor with units of conductivity, $\omega(2\pi f)$ is the angular frequency and $n$ is the power law exponent in the range from 0 to 1. For $n = 0$, the electrical conductivity is frequency independent (DC process), whereas for $n > 0$, the conductivity is frequency dependent (AC process) [23]. For the present system, the value of the exponent $n$ varied from 0.41 to 0.77, implying that the conduction mechanism in the studied samples was AC process dominated by the hopping of charge carriers [24]. Fig. 6 shows the AC conductivity ($\log\sigma_{ac}$) as a function frequency. All the samples show an increase in $\sigma_{ac}$ with increasing frequency normal behaviour of ferrite materials. The conduction mechanism can be explained in terms of electron hopping between Fe$^{2+}$ and Fe$^{3+}$ ions at octahedral sites. Higher frequencies enhanced the hopping rate of the charge carriers, resulting in an enhancement of the conduction process and hence, an increase in the
conductivity. In addition, at high frequencies, the conductivity remains constant because the hopping can no longer follow the changes in the external applied field and rather lags behind it [25]. The Fe$^{2+}$ concentration plays an important role in the mechanisms of conduction and dielectric polarization. Thus, the highest values of $\varepsilon'$ and $\sigma_{ac}$ observed for the $x=0.75$ sample can be attributed to the enhanced formation of Fe$^{2+}$ ions. Conversely for the other compositions the decrease in $\sigma_{ac}$ is attributed to a lower concentration of Fe$^{2+}$ ions at octahedral sites.

3.4 Magnetic properties

Room temperature hysteresis loops for all samples showed the characteristic ‘S’ shaped loops (Fig. 7) which indicates the soft nature of the prepared samples. The magnetic data, saturation magnetization ($M_s$) and coercivity ($H_c$) determined from the hysteresis loop data are presented in Table 1. It can be seen from that the $M_s$ values increased up to $x=0.5$ and then decreased. The initial increase in $M_s$ with increasing Zn content is due to the increase in the sublattice magnetic moment, which can be explained using Neel’s collinear two sublattice model [26]. Neel considered three types of magnetic interactions: AA, AB and BB. AB interactions align the magnetic spins of the A site in one direction and B site in the opposite direction: therefore, the net magnetic moment ($M_s$) of the lattice is the difference between the magnetic moments of the B ($M_B$) and A ($M_A$) sites i.e $M_s = M_B - M_A$. The magnetic moment of each composition depends on the distribution of magnetic and nonmagnetic ions on A and B sites in the spinel structure [17]. In the Mg-Zn ferrite Fe$^{3+}$ and Mg$^{2+}$ occupy both A and B sites, whereas nonmagnetic Zn$^{2+}$ ions prefer to occupy A sites. Zn$^{2+}$ substituted on A sites shifts some of the Fe$^{3+}$ ions from A sites, to B sites thereby decreasing $M_A$ and increasing $M_B$. This results in an increase in $M_s$ up to $x=0.5$. According to the random canted model, substitution of diamagnetic cations in one sublattice leads to spin canting in the other sublattice resulting in a decrease in the magnetization. The reason for the decrease in
magnetization beyond $x = 0.5$ is that the magnetization of the A-sublattice is so small that the A–B interaction is very weak and only the B–B interaction is significant, which in turn disturbs the parallel arrangement of the spin magnetic moments on the B-site and hence spin canting occurs. Neel’s two-sublattice collinear ferrimagnetism was observed for our system up to $x \leq 0.5$ and beyond this limit, a three-sublattice non-collinear spin canting condition is predominant. The existence of canted spin gives rise to the Yafet–Kittel angle. The narrow hysteresis loops of our samples indicate the low coercivity values indicating that this material can be easily demagnetized for electromagnetic applications [24].

4. Conclusion

Zinc substituted magnesium ferrite samples were prepared using a solution combustion method. All the samples showed a single-phase cubic spinel structure. The morphology of the samples showed polyhedral grains with an increase in grain size as a function of increasing Zn concentration. The dielectric constant, dielectric loss tangent and AC conductivity were found to have minimum values for a Zn$^{2+}$ concentration of $x = 0.50$. The saturation magnetization increased with increasing Zn$^{2+}$ content up to $x = 0.50$ due to a strong AB interaction and decreased thereafter due to spin canting. Hence, we can conclude from the dielectric and magnetic studies of Zn doped Mg ferrite, that $x = 0.50$ is an optimum composition achieving relatively high magnetization, and low dielectric constant, dielectric loss, and AC conductivity.

Acknowledgments

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References:


Figure caption

**Fig. 1** Powder XRD patterns of Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrites sintered at 1050 °C

**Fig. 2** SEM micrographs of the fracture surfaces of Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$

**Fig. 3** EDX spectra of Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$

**Fig. 4.** Frequency dependence of the dielectric permittivity of Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$

**Fig. 5.** Frequency dependence of the loss tangent of Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$.

**Fig. 6.** Frequency dependence of the ac conductivity of Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$.

**Fig. 7.** Magnetization versus field behaviour of Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$. 
Table 1 Composition dependence of lattice parameter \((a)\), crystallite size \((D)\), grain size, X-ray density \((d_x)\), bulk density \((d_b)\), apparent porosity, magnetization \((M_s)\) and coercivity \((H_c)\) of \(\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4\) at room temperature.

Table 2 Elemental composition for \(\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4\) as determined by EDX analysis.
Table 1

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<th>d_b (gm/cc)</th>
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<th>Apparent porosity (1-d_b/d_x) (%)</th>
<th>M_s (emu/g)</th>
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Table 2

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Figures

Fig. 1
Fig. 2
Fig. 3
Fig. 5
Fig. 6
Fig. 7