Tuning of physical properties of multifunctional Mg-Zn spinel ferrite nanocrystals: a comparative investigations manufactured via conventional ceramic versus green approach sol-gel combustion route

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Abstract
This work focused on the impact of synthesis routes on the structural, microstructural, magnetic, electrical and dielectric characteristics of Mg₁₋ₓZnₓFe₂O₄ (x = 0.00, 0.25, 0.50, 0.75, and 1.00) nanocrystals manufactured via the ceramic and green approach sol–gel route. The powder X-ray diffraction (XRD) analysis reveals that the entire synthesized ferrite solids crystallize in single phase spinel structure. The XRD outcomes highlight the impact of the synthesis routes and Zn²⁺ replacement on the morphology, crystallite size and structural parameters of magnesium nano-ferrites. The transmission electron microscopy (TEM) images illustrate that the process of synthesis causes extensive lessening of grain and crystallite sizes. The magnetic study reveals that the magnetic properties of magnesium ferrite can be tuned by zinc substitution. The saturation magnetization (Ms), retentivity (Mr), coercive force (Hc) and magneton number diminutions meaningfully with the replacement of diamagnetic Zn²⁺ ions in Mg-ferrite for both the synthesized systems. The deterioration of magnetic parameters with Zn²⁺ substitution can be clarified on the base of the random spin canting model. Likewise, the magnetic parameters, enhanced meaningfully for sol-gel derived samples this can be attributed due to decline of crystallite size effect. The DC electric resistivity displays NTCR behaviour like ideal semiconducting materials for all the produced samples. The DC resistivity values of sol-gel produced samples were found to be little bit higher than that of ceramic derived samples. The experimental dielectric constant as a function of frequency behaviour can be elucidated with the support of the heterogeneous model of the polycrystalline structure of ferrites. The dielectric constant and loss tangent decreases with Zn²⁺ content for both the systems. The dielectric constant enhances for sol-gel derived samples; however, lower values of loss tangent were found. The obtained outcomes can be suitable for multifunctional applications in electronics devices and biomedical field.

1. Introduction

Whenever we talk about magnetic materials, the first solid that comes into our mind is spinel ferrite ceramic material. The spinel ferrite materials (M–Fe₂O₄, M-divalent metal cations) are widely investigated solid oxide materials across the globe because of versatile electro-magnetic assets [1]. Even after nearby 90 years of disclosure, spinel ferrite persisted as the most frequently utilized ferromagnetic material [2]. These materials have a wide spectrum of potential applications such as microwave absorbing materials [3], magnetic resonance
imaging (MRI) contrast agents [4], data storage systems [5], magnetic induction hyperthermia [6], anticorrosive paints [7], multi-layer chip inductor [8], sensors [9], environmental perspectives [10] and many more.

Now days, it is universally believed fact that, the properties of nanomaterials are strangely diverse than that of their bulk mates. This is primarily a direct result of the nanometer dimension of the materials which makes them: huge fraction of superficial atoms, an increased surface area to volume ratio and quantum confinement phenomenon, spatial confinement, reduced imperfections. Size impacts establish a peculiar and fascinating characteristic of nanomaterials [11, 12]. The impacts determined by crystallite size relate to the development of structural, microstructural, thermodynamic, electromagnetic and chemical properties of these finite systems with the varying crystallite size [13].

Currently, ecofriendly spinel ferrite nanoparticles have numerous potential applications in medical sciences [14], magnetic diagnostic and treatment devices [15], catalysts [16], lithium-ion batteries [17], pollution control [18] and water purification process [19]. Between the spinel ferrites, magnesium ferrite (MgFe₂O₄) is ecofriendly solid which has a partly inverse spinel structure with semiconducting possessions [20]. It can be considered as a diluted ferrimagnetic solid whose extent of inversion and properties can be tuned by the route of synthesis and synthesis circumstances [21]. The replacement of numerous diamagnetic ions such as Ba²⁺, Ca²⁺, Zn²⁺, Cd²⁺, Al³⁺, Cr³⁺, Ti⁴⁺, Zr⁴⁺ etc, into a magnesium ferrite matrix may enhance electric, dielectric and magnetic properties [22–25].

Among the transition metals, non-magnetic zinc (Zn²⁺) is a very promising and exciting candidate. The magnetic properties of Zn²⁺-substituted ferrites have attracted considerable attention on account of the importance of these materials for high-frequency devices and soft magnetic applications [26]. It was reported that Mg-Zn mixed ferrite nanoparticles can be appropriate for hyperthermia applications [27]. Also, it was detected that the Curie temperature falls down with substitution of Zn²⁺ - concentration in Mg-Zn spinel ferrite [28].

It is well acknowledged fact that the properties of spinel ferrites can be easily tuned by the process of synthesis [29]. The designing of materials in particular fashion so as to get desired properties is an imperative task. Also, the accomplishment of its practical applications is subject to the ability of monitoring the crystallite size. There are numerous numbers of methods available to acquire the spinel ferrites in bulk as well as nano-dimensions, including conventional ceramic technique to modern wet-chemical techniques [30]. High calcination temperatures and powerful ball-milling are essential to synthesize sample by conventional techniques. As a substitute, different wet chemical methods have been developed to fabricate spinel ferrite nano-metric scale powders [31]. Owing to superior physical properties of nano as related to their bulk counterpart, diverse modified wet chemical approaches are in improvement [32–34].

Over the most recent couple of years, the sol-gel combustion technique is frequently used to synthesize spinel ferrite nanoparticles using metal nitrates and organic compounds such as, citric acid, glycine, urea, ascorbic acid, alanine, L-arginine, etc as a fuel or firing agent [35–37]. The fuel is mixed with metal nitrate solutions to improve the effectiveness of the combustion reaction. In this reaction, we have used green approach, the metal nitrates as an oxidizing agent also cation source and the normal coconut water is used as a fuel and chelating agent. Coconut water is an exceptional natural source of glucose and sucrose also contains a liquid with maximum amount of water [38]. In order to avoid extremely poisonous and harmful vapors throughout the combustion process coconut water is used as a fuel in this reaction. Now a days, several green approaches are in progress to fabricate different oxide materials [39, 40].

S.Hajarpour, et al investigated the magneto-structural properties of Mg-Zn soft ferrites nanocrystals synthesized through glycine–nitrate combustion route. It was observed that the saturation magnetization enhances for the low Zn²⁺ concentration and decreases afterwards [41]. Biocompatible nanoparticles of Mg-Zn spinel ferrite nanoparticles were synthesized through solvothermal reflux technique and its photocatalytic and superparamagnetic nature was elucidated by A.Manohar et al [42]. H. Liu et al explored the magnetic induction heating properties of Mg-Zn ferrites synthesized by co-precipitation technique [28]. H. Saqib et al inspected the structural, vibrational, electrical, and magnetic characteristics of Mg-Zn spinel ferrite nanoparticles fabricate by co-precipitation method. An increase in electrical resistivity with increasing Mg-concentration was observed [43]. The comprehensive magneto-structural and toxicity examinations of Mg-Zn and Cu-Zn mixed ferrites for magnetic resonance imaging thermometry applications were carried out by Alghamdi et al [44].

The literature survey recommends that extensive research is focused on the structure and physico-chemical properties of mixed Mg-Zn ferrite nanoparticles [45–47]. But, still the outcome of different synthesis routes on crystallite size, structure and consequently on the electrical, dielectric, optical and magnetic characteristics is yet missing.

In this work, we made a systematic investigation of the structural, microstructural, magnetic, electrical and dielectric properties of MgₓZnₓFe₂O₄ for x = 0.00, 0.25, 0.50, 0.75, and 1.00 samples synthesized by two different techniques i.e. via conventional ceramic and green approach sol-gel combustion. The comparative study of various physical properties of Mg-Zn mixed ferrite in the light of crystallite size is also discussed.
2. Experimental details

Mixed Mg-Zn nanoparticles with a chemical formula of Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ for $x = 0.00, 0.25, 0.50, 0.75,$ and 1.00 were produced by conventional ceramic and green approach sol-gel combustion techniques.

(a) Ceramic technique:
Analytical grade (AR) oxides of respective ions, i.e. magnesium oxide (MgO), zinc oxide (ZnO) and ferric oxide (Fe$_2$O$_3$) with high concentration were purchased from Merck. These oxides were accurately measured on an electronic balance and mixed together consistent with stoichiometric proportions. The mixed oxides were finely crushed for 3–4 h using agate mortar and pestle. The pulverized powder is then heat treated at 1020 °C for 24 h in a controllable muffle furnace and cooled steadily to normal temperature. The sintered powder is now milled for 3–4 h and lastly sintered at 1100 °C for 24 h followed by slow cooling. The sintered powders are hard-pressed into cylindrical pellet form using hydraulic press and by applying a pressure 6 ton cm$^{-2}$. Lastly, sintered powder and pellets were used for characterizations and for the measurement of electrical, dielectric and magnetic properties.

(b) Green sol-gel combustion technique:
The raw materials in the form of nitrates i.e. magnesium nitrate Mg(NO$_3$)$_2$·6H$_2$O, zinc nitrate Zn(NO$_3$)$_2$·6H$_2$O, ferric nitrate Fe(NO$_3$)$_3$·9H$_2$O, ammonium hydroxide solution (NH$_4$OH), were procured from Merck with high purity of 99.9%. For the chelating of metal nitrates, natural coconut water was (50 ml) used as a fuel or chelating agent. Homogeneous solutions of respective metal nitrates and coconut water in the stoichiometries quantities were prepared by dissolving it in 100 ml deionized water distinctly by persistent stirring. These organized solutions were mixed together and stirred for 30 min to get a clear homogeneous solution. Later, the pH of the solution was preserved to the neutral value, i.e. pH = 7 by adding ammonia solution dropwise. After continuous thermal treatment and stirring at 90 °C, for the time period of 4 h the solution gets transformed from sol to the viscous gel. After some time, the auto-combustion reaction takes place and quickly the gel converts into a fluffy powder. The loose flocy powder was composed and pulverized with the aid of pestle mortar. The crushed powder was exposed to a thermal treatment at the temperature of 650 °C for 5 h. The processed powder samples were utilized for the characterizations. Heat-treated powder samples were mixed with polyvinyl alcohol (PVA) agent as a binder and pressed into cylindrical tablet form (10 mm diameter and less than 3 mm thickness) by the isostatic pressing method under the pressure of 550 kg cm$^{-2}$. The tablets were heat treated in an oven at 400 °C for 2 h for the eradication of PVA. The cylindrical tablets were utilized for additional electric and dielectrical estimations.

2.1. Characterizations
Several analytical techniques were used for the characterizations of manufactured spinel ferrite materials. The phase identification of the Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ samples was characterized by powder X-ray diffractometer (Ultima IV, Rigaku Corporation, Japan). The surface topography and internal structure were scrutinized utilizing transmission electron microscope (TEM, Philips CM200) instrument. The surface analysis was examined with ‘Brunauer–Emmett–Teller (BET)’ technique via recording the ‘N$_2$’ adsorption-desorption isotherm’. The ‘Quantachrome’ instrument with v-5.2 model was utilized to trace the isotherm. The room temperature magnetic properties of the produced ferrites were calculated from the $M$–$H$ loops, measured with a pulse field hysteresis loop technique (Magnata Company) with an extreme applied field of 7 kOe. DC electrical conductivity mechanism in prepared ferrites was evaluated by studying their DC electrical resistivity. The typical and easy two-probe equipment was employed to examine electrical characteristics of the pelletized ferrite samples. The DC electrical resistivity was calculated in the temperature scales from ~472 K—975 K. The room temperature dielectric characteristics were completed operating LCR-Q meter (Hioki 3532-50, Japan) as a component of frequency.

3. Results and discussion

Figures 1(a) and (b) displays the powder XRD diffractograms of Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ for $x = 0.00–1.00$ spinel ferrites produced by conventional ceramic route contrasted with the green sol-gel combustion route correspondingly. Entire reflections appeared in diffraction patterns agreeably indexed with monophasic cubic spinel structure with space group $Fd-3m$ (JCPDS-88-1935) deprived of any contamination phase [48]. The observed Bragg’s reflections for sol-gel synthesized samples as shown in figure 1(b) are slightly broader than that of ceramically synthesized samples, confirming the added nanocrystalline nature of the formed samples. The occurrence of planes (111), (220), (311), (222), (400), (422), (511), (440) and (533) in the XRD diffractograms

\[ x = 0.00, 0.25, 0.50, 0.75, \text{ and } 1.00 \]
exposes the cubic spinel structure of all the samples. It is also evident that all the reflection peaks are highly intense besides sharp-edged thus, the samples are single phase in nature.

From figure 2 it is clearly seen that, the intensity of reflected planes of sol-gel synthesized sample is very much higher than that of ceramically derived solids, indicating growth in the proportions of crystallinity in the material [49].

As well, from figure 2 it is evidenced that modulated shifting of 2θ values takes place for (311) plane with zinc substitution due to microstructural variation. Ceramic produced samples shows distinctive shift in 2θ values than that of sol-gel derived samples which may be due to change in the crystallinity and micro-strain of the material or incorporation of defects [50]. The shifting of peak towards lower 2θ values with Zn²⁺ concentration indicates expansion of unit cell volume. As the peak shift for sol-gel derived samples is in a lesser amount of 2θ ensuring the improved stability of the crystals. The average crystallite size (t) of the Mg-Zn ferrite powders was estimated by using the most intense peak (311) and using the well-known Debye-Scherer’s formulation [51, 52].

Figure 3 shows the distinction of average crystallite size with Zn²⁺ concentration x in comparison with two different synthesis routes. It was observed that we got crystals in the range of 54.82 nm to 59.77 nm for ceramic resultant samples, however, crystals of size 17.65 nm to 27.49 nm for sol-gel derived samples.

Figure 4 illustrates the compositional reliance of lattice constant (a) concerning to the Zn²⁺ replacement for respective synthesis route. It is noticed from figure 4 that, lattice constant (a) shows the increasing trend with upsurge in the Zn²⁺ content x following the Vegard’s regulation i.e. the replacement of Mg²⁺ ions (0.66 Å) by higher ionic radius Zn²⁺ (0.82 Å) ions [53]. The identical tendency was observed for the both systems. The ceramically synthesized samples tend to exhibit higher values of the lattice constant due to the existence of defects and impurities. Such defects are introduced through sample synthesis and differ according to the process of synthesis and reagents used [54]. Rendering to the reports, the lattice constant and crystallite size are directly

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Figure 1. (a). Powder-XRD diffractograms of Mg₁₋ₓZnₓFe₂O₄ samples synthesized by ceramic route. (b). Powder-XRD diffractograms of Mg₁₋ₓZnₓFe₂O₄ samples synthesized by sol-gel route.
Figure 2. Magnified XRD graphs viewing shift in 2\(\theta\) values and intensity variation for (311) plane.

Figure 3. Variation of average crystallite size with Zn\(^{2+}\) concentration \(x\).

Figure 4. Variation of lattice constant with Zn\(^{2+}\) concentration \(x\) for two different synthesis routes.
interconnected [55]. The lattice constant of pristine MgF$_2$O$_4$ and ZnFe$_2$O$_4$ solids and the observed increasing trend per Zn$^{2+}$ replacement well resembles with the stated data in the literature [56].

The X-ray density ($dx$) entities were calculated by means of unit cell volume and molecular weight [57]. The compositional discrepancy of X-ray density values is revealed in figure 5. The growing tendency was observed for the values of $dx$ for both the systems. The increment of the $dx$ values with increasing Zn$^{2+}$ ions replacement is may be caused due to the rise in the molecular weight of the Mg-Zn compositions. The equivalent inclination and slight difference in X-ray density were observed for both the systems.

To inspect topographical information, the TEM images are observed for the selective produced samples. It is perceived from all the TEM images that the samples are agglomerated in spherical and cubical profile in nano-metric scale. A clear difference is observed among the ceramic and sol-gel derived samples. Figures 6 (a)–(b) and figures 7(c)–(d) shows the TEM morphology of $x = 0.00$ and $x = 0.50$ samples manufactured via ceramic and sol-gel techniques correspondingly. The figures 6(e)–(f) and figures 7(g)–(h) are crystallite size distribution graph of clearly measurable nanoparticles. The histogram of the size distribution is characterized by a Gaussian
function (solid line). The TEM outcomes are in upright agreement with the size reduction detected using XRD analysis discussed earlier.

Brunauer–Emmett–Teller (BET) analysis was used to determine the surface related parameters of the typical samples. The N2 adsorption-desorption isotherm curves of pure magnesium ferrite prepared by ceramic and sol-gel auto combustion route are shown in figure 8.

The different parameters such as specific surface area, Average Pore diameter and Pore volume were determined from the analysis. The values of these parameters are noted in the table 1.

The specific surface area of the magnesium ferrite prepared by ceramic and sol-gel auto combustion route was found to 1.357 m2 gm−1 and 34.228 m2 gm−1 respectively. It is well known that the surface area of the materials tremendously increases when it changes from bulk from to nano form. Thus, in the present case the major difference in the surface area was observed. In addition to the specific surface area, the average pore diameter and pore volume of the magnesium ferrite prepared by ceramic and sol-gel auto combustion route was also measured by Barett-Joyner-Halenda (BJH) analysis. The average pore diameter of the magnesium ferrite prepared by ceramic and sol-gel auto combustion route was found to 4.12 nm and 8.69 nm respectively. The pore volume of the magnesium ferrite prepared by ceramic and sol-gel auto combustion route was found to 0.0198 c.c./gm and 0.0755 c.c./gm respectively.

Figures 9(a) and (b) demonstrates M–H loops (recorded at the room temperature) of Mg1−xZnxFe2O4 (x = 0.00–1.00) spinel ferrites produced via ceramic versus the sol-gel route individually. The magnetic entities alike saturation magnetization (Ms), retentivity (Mr) and coercive force (Hc) were derived from M–H loops. As the zinc concentration rises the Ms values decrease pointedly for both the systems as shown in figures 9(a) and (b). The diminution in Ms values was accredited to the replacement of non-magnetic Zn2+ ions. Actually, the magnetic properties of spinel ferrites are very much reliant on the occupancy of cations in the tetrahedral and octahedral sites [58].

In few literatures, it was observed that the Ms values initially upsurges for low Zn2+ content and then decreases, which was explained on the basis of Neel’s two sublattice model [59]. In this case, we found that the Ms values decrease steadily with Zn2+ concentration for all the samples. This observed trend could be understood on the basis the random spin canting model, substitution of diamagnetic cations in one sublattice of ferrimagnet originates spin canting in the further sublattice responsible for the reduction in the overall magnetization per formula unit. This can be accredited to the magnetization of A-sublattice are so diluted that the A–B exchange mechanism is no further stays dominant and thus B–B sublattice interaction becomes noteworthy. This B–B sublattice interaction interrupts the parallel alignment of spin magnetic moments on the octahedral [B]-site and hereafter canting of spin arises. Neel’s three-sublattice non-collinear spin canting model is principal for the increasing Zn2+ content samples and henceforth decrease in Ms values [60]. Analogous
outcomes for Mg-Zn sol-gel derived solids were found in the literature manufactured by co-precipitation route [61].

Now in comparison with the process of synthesis route and crystallite size, it was found that the magnetic entities were significantly enhanced for sol-gel derived solids. Figure 10 shows the juxtapose of $M_s$ values with different concentrations of Zn$^{2+}$ for ceramic and sol-gel routes.

It was seen that, as the crystallite size declines the saturation magnetization was seen to increment. Henceforth, sol-gel derived shows superior magnetic properties as compared to ceramic derived solids. The pure ZnFe$_2$O$_4$ sample ($x = 1.00$) shows completely paramagnetic nature which has crystallite size of 59 nm obtained by ceramic technique. For sol-gel derived pure ZnFe$_2$O$_4$ solid, the crystallite size reduces up to 17 nm and therefore as expected the sample show typical ferromagnetic nature ($M_s = 21.22$ emu g$^{-1}$ and $H_c = 197.12$ Oe). The smaller values of magnetization for ceramic derived samples can be explained on the base of growing grains and its size. In light of the grain development, grain traps the between granular pores. Since, during the grain development, the pores among the grains are trapped. This inter-granular sponginess is may be accountable for the diminution of magnetic entities [62, 63].

The coercive force ($H_c$) overall increases with the Zn$^{2+}$ content (as depicted in figure 11). Likewise, the $H_c$ values of sol-gel derived samples are superior than ceramic derived solids. The upsurge in $H_c$ values may be attributed to the conversion from the unblocked to the blocked state, i.e. due to withdrawal from the super-paramagnetic state of the nanocrystals [64]. This conversion happens in lesser nanoparticles when the anisotropy energy governs the thermal energy in the system. Generally, the coercivity primarily depends upon two chief parameters, such as, crystallite size and anisotropy constant [65]. The crystallite size decreases for sol-gel synthesis and it results to increase in the coercivity value. Consuming the values of saturation magnetization, the magnetic moment per formula unit, $n_B$ (in Bohr magneton) was estimated [66].
Figure 12 shows the discrepancy of magneton number for the two different synthesis routes with Zn$^{2+}$ content $x$. The magneton number values were found to be higher for sol-gel derived samples. The magneton number ($n_B$) values decrease with Zn$^{2+}$ content for both the systems.

Figure 9. (a) M-H hysteresis curves of Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ samples synthesized by ceramic route (b). M-H hysteresis curves of Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ samples synthesized by sol-gel route (Inset shows magnified image clearly indicating increase in coercive force).

Figure 10. Saturation magnetization ($M_s$) versus Zn$^{2+}$ concentration $x$. 
The anisotropy constant ($K$) also decreases with Zn$^{2+}$ concentration $x$ for two different synthesis techniques as depicted in figure 13. The $Mr$ values don’t show linearity behavior, since the large ionic radii of zinc favor a normal spinel geometry over the mixed spinel geometry of magnesium ferrite nanocrystals which reasons a loss of magnetic energy that results in random remanent values. Also, the microstructural defect influences the coercivity and retentivity of the material [67].

The DC electrical resistivity investigations of the produced Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ samples were estimated as a component of temperature. Figures 14(a) and (b) shows the discrepancy of the logarithm of resistivity ($\log \rho$) as a component of the reciprocal of temperature ($1000/T$) for ceramic and sol-gel route individually.

It is evident from figures 14(a) and (b) that the dc resistivity fall off with rising thermal treatment conforming Arrhenius relation for both the systems [68]. It was observed that, as Zn$^{2+}$ content increases from $x = 0.0$ to 0.75 the dc resistivity values increase. However, the dc resistivity values of $x = 1.00$ i.e. pristine ZnFe$_2$O$_4$ solid was found pointedly lower. The same trend is observed for both the systems.

The observed values of resistivity with rising temperature can be accredited to the to the consequence of ferromagnetic ordering on conduction phenomenon. This is attributed to the destruction of spontaneous magnetization and the variation in additional charge carrier concentration in the region of Curie transition temperature [69]. In ferrites, being magnetic semiconductors, resistivity in the low temperature called as region I is attributed to impurities and is extrinsic in nature. At high temperatures, the resistivity called as region II is intrinsic in nature and is due to the electron hopping mechanism among Fe$^{3+}$ to Fe$^{2+}$ ions. This linear reduction in resistivity values with temperature was accredited to the thermally activated mobility of the charge transporters. It implies that the discontinuity at Curie temperature is accredited to the magnetic transformation
from well-ordered ferrimagnetic state to disordered paramagnetic state, which contains dissimilar activation energies. The resistivity of ferrites, in over-all, relies upon the density, porosity, grain size, grain boundary area, defects and chemical composition of the material [70, 71].
The dc resistivity values of sol-gel prepared solids were found to be a little bit higher than that of ceramic derived solids. The detected behaviour can be understood on the foundation of size of the nanocrystals. The crystallites of lower nano-grained assembly were attained through the sol-gel route. It was well acknowledged fact that the smaller crystallite size indicates a growth of the insulating surface on the grain boundaries, which normally accounts for huge electrical resistance of the polycrystalline materials. The other fact is that the porous structure of these samples hinders the motion of charge carriers leading to an increase in the resistivity.

This observed negative temperature coefficient resistance (NTCR) behaviour of these synthesized ferrites makes them useful for high frequency device applications wherever eddy current losses become vital factor.

The higher values of the DC resistivity are because of compositional stoichiometry, better crystal structures and the enhanced microstructures attained by the sol-gel technique. A microstructure with smaller grain contains a greater number of grain boundaries. The grain boundaries are regions of discrepancy among the energy states of the in-line grains and hence, acts as blockades to the movement of electrons. The high resistivity observed in the sol-gel derived samples is thus credited to the small grain size.

Figures 15(a) and (b) represents the disparity of dielectric constant as a component of frequency (log f) manufactured by two different synthesis techniques. It can be observed in both cases that the dielectric constant was higher at low frequency spectrum and it decreases exponentially with increasing frequency. The frequency dependence dielectric constant can be elucidated with the support of the heterogeneous model of the polycrystalline structure of ferrites suggested by Koops. The values of dielectric constant decreases pointedly with Zn$^{2+}$ concentration for both the systems. The cause for this observation is the diminution in the number of Fe$^{2+}$ ions owing to the substitution of the Zn$^{2+}$ dopants possibly at the octahedral sites. Henceforth, because of interruption of electron transfer between Fe$^{2+}$ and Fe$^{3+}$ by the dopants, a reduced space charge polarization is projected to decrease the dielectric constant.
In view of synthesis techniques, it can be observed from figures 15(a) and (b) that the dielectric constant of sol-gel derived samples is greater than that of the ceramically synthesizes samples. The XRD and TEM examinations suggested that the crystallite size of the sol-gel samples reduced than that of ceramic samples. The dielectric constant increases with decrease in crystallite size as reported in the literature [77].

Figures 16(a) and (b) shows the discrepancy in the dielectric loss factor of Mg–Zn ferrites manufactured via the two different routes. The dielectric loss tangent (tan δ) demonstrates same tendency as that of dielectric constant. The tan δ values decrease as the frequency increases. This deterioration designates the usual behavior of spinel ferrite solids. It occurs when the hopping frequency of electric charge carriers could not act in accordance with the modification of the exterior applied alternating electric field beyond a certain critical frequency. Also, the tan δ values of sol-gel derived samples were lower than that of ceramic derived samples due to decrease in crystallite size. The mixed Mg–Zn ferrite exhibit a lower value of dielectric constant and dielectric loss as compared to other spinel ferrites due to the presence of Zn$^{2+}$ ions in the samples [78]. The obtained dielectric behaviour can be much beneficial for the fabrication of electronic appliances that can be operated in a wide frequency range.

4. Conclusions

A sequence of nano-sized crystals of Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ ($x = 0.00, 0.25, 0.50, 0.75,$ and $1.00$) spinel ferrites have been manufactured by ceramic and the facile ecofriendly sol-gel route. XRD diffractograms are in accordance with the cubic spinel structure with space group Fd-3m without any impurity traces. The average sizes of the crystals were estimated to be in the range of 54–59 nm for ceramic and 17–27 nm for sol-gel derived solids. The impact of the synthesis procedure on the internal structure of the produced ferrites inspected by TEM.
observations, which well supported the XRD outcomes. The process of synthesis meaningfully enhances the magnetic, electrical and dielectric characteristics of synthesized Mg-Zn ferrite solids. The magnetic study revealed that all the magnetic entities decreases with zinc replacement. The sol-gel derived solids showed superior magnetic properties than that of ceramic derived solids. For pure magnesium ferrite, the highest value of $M_s = 89.69 \text{ emu g}^{-1}$ for sol-gel and $M_s = 68.38 \text{ emu g}^{-1}$ for ceramic route were found. Magnetic data showed that by reducing crystallite size, $M_s$ and $H_c$ values significantly enhances. The dc electrical resistivity investigations confirmed the ideal semiconducting nature of the produced samples. The dc resistivity values overall increase with the zinc substitution for both the systems, however, the pure ZnFe$_2$O$_4$ solid shows highly resistive nature. The dc resistivity values of sol-gel derived solids were higher than that of ceramic derived solids which can be attributed to lower grain sizes. The dielectric constant and loss tangent both decrease with growing frequency and zinc concentration in accordance with Koops model. The sol-gel samples show improved dielectric constant values which can be elucidated on the base of reduced crystallite size effect. These investigations evidenced that the physical properties of spinel ferrites can be easily tuned by the process of synthesis by controlling the crystallite size. The obtained magnetic properties of this mixed Mg-Zn spinel ferrite nanoparticles make them beneficial for potential applications in biomedical sciences. The obtained electrical and dielectric properties can be valuable for the fabrication of electronic appliances.

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References

[1] Mathew D S and Juang R-S 2007 An overview of the structure and magnetism of spinel ferrite nanoparticles and their synthesis in microemulsions Chem. Eng. J. 129 51–65
[2] Sugimoto M 1999 The past, present, and future of ferrites Journal of the American Ceramic Society 82 269–80
[3] Xie J L, Han M, Chen L, Kuang R and Deng L 2007 Microwave-absorbing properties of NiCoZn spinel ferrites J. Magn. Magn. Mater. 314 37–42
[4] Amiri S and Shokrollahi H 2013 The role of cobalt ferrite magnetic nanoparticles in medical science Materials Science and Engineering: C 33 1–8
[5] Hu W, Qin N, Wu G, Lin Y, Li S and Bao D 2012 Opportunity of spinel ferrite materials in nonvolatile memory device applications based on their resistive switching performances J. Am. Chem. Soc. 134 14656–61
[6] Iftekhar A, Islam M U, Awam M S, Ahmad M, Naseem S and Iqbal M A 2014 Synthesis of super paramagnetic particles of Mn$_{1-x}$Mg$_x$Fe$_2$O$_4$ ferrites for hyperthermia applications J. Alloys Compd. 600 146–59
[7] Abu Ayana Y M, El-Sawy S M and Salah S H 1997 Zinc-ferrite pigment for corrosion protection Anti-Corrosion Methods and Materials 44 381–8
[8] Li B, Yue Z-X, Qi X-W, Zhou J, Gui Z-L and Li L-T 2003 High Mn content NiCuZn ferrite for multiplayer chip inductor application. Materials Science and Engineering: B 99 252–4
[9] Sutka A and Kärils A G 2016 Spinel ferrite oxide semiconductor gas sensors Sensors Actuators B 222 95–105
[10] Fardoud T, Moradnia F, Mostafaei M, Alishari Z, Faramarzi V and Ganjkhani S 2019 Biosynthesis of MgFe$_2$O$_4$ Magnetic Nanoparticles and Their Application in Photodegradation of Malachite Green Dye and Kinetic Study Nanochem. Res. 4 86–93
[11] Murty B S, Shankar P, Raj B, Rath B B and Murday J 2013 Textbook of Nanoscience and Nanotechnology (Germany: Springer-Verlag Berlin Heidelberg)
[12] Kulkarni S K 2014 Nanotechnology: Principles and Practices (Berlin: Springer)
[13] Bhushan B 2017 Springer Handbook of Nanotechnology (Berlin: Springer)
[14] Amiri M, Salavati-Niasari M and Akbari A 2019 Magnetic nanocarriers: evolution of spinel ferrites for medical applications Adv. Colloid Interface Sci. 265 29–44
[15] Bae S, Lee S W, Hirukawa A, Takemura Y, Jo Y H and Lee S G 2008 AC magnetic-field-induced heating and physical properties of ferrite nanoparticles for a hyperthermia agent in medicine IEEE Trans. Nanotechnol. 8 86–94
[16] Liu P, He H, Wei G, Liang K, Qi F, Tan F, Tan W, Zhu J and Zhu R 2016 Effect of Mn substitution on the promoted formaldehyde oxidation over spinel ferrite: catalyst characterization, performance and reaction mechanism Appl. Catalysis B 182 476–84
[17] Masoud E M 2013 Improved initial discharge capacity of nanostructured Ni-Co spinel ferrite as anode material in lithium ion batteries Solid State Ionics 253 47–52
[18] Satyanarayana L, Reddy K M and Manorama S V 2003 Nanosized spinel NiFe$_2$O$_4$: a novel material for the detection of liquefied petroleum gas in air Mater. Chem. Phys. 82 21–6
[19] Kefeni K K, Bhekie B M and Titus A M M 2013 Application of spinel ferrite nanoparticles in water and wastewater treatment: a review Sep. Purif. Technol. 188 399–422
[20] Banuai K K, Kour G, Kaur B and Kulkarni S D 2013 Effect of cation distribution on structural and magnetic properties of Dy substituted magnesium ferrite J. Magn. Magn. Mater. 327 159–66
[21] Thanakachan S, Binu P J, Xavier S and Mohammed E M 2013 Effect of neodymium substitution on structural and magnetic properties of magnesium ferrite nanoparticles Phys. Scr. 87 025701

[22] Kaur M, Rana S and Tarasikha P S 2012 Comparative analysis of cadmium doped magnesium ferrite $\text{Mg}_{1-x}\text{Cd}_{x}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6$) nanoparticles Ceram. Int. 38 4319–23

[23] Ateia E, Tkala E and Mohamed A T 2017 Physical and magnetic properties of (Ba/Sr) substituted magnesium nano ferrites Appl. Phys. A 123 631

[24] Raghavendra M, Ravinder D and Veerasamaih P 2015 Electrical resistivity studies of Cr doped Mg nano-ferrites Materials Discovery 2 30–4

[25] Diao Y, Yan Z, Guo M and Wang X 2018 Magnetic multi-metal co-doped magnesium ferrite nanoparticles: an efficient visible light-assisted heterogeneous Fenton-like catalyst synthesized from saprolite laterite ore J. Hazard. Mater. 344 829–38

[26] Choodamani C, Rudraswamy B and Chandrappa G T 2016 Structural, electrical, and magnetic properties of Zn substituted magnesium ferrite Ceram. Int. 42 10565–71

[27] Sharma R, Thakur P, Kumar M, Barman P B, Sharma P and Sharma V 2017 Enhancement in AB super-exchange interaction with Mn$^2+$ substitution in Mg:Zn ferrites as a heating source in hyperthermia applications Ceram. Int. 43 13661–9

[28] Liu H, Li A, Ding X, Yang F and Sun K 2019 Magnetic induction heating properties of Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrites synthesized by co-precipitation method Solid State Sci. 93 101–6

[29] Diodati S, Pandolfo L, Caneschi A, Gialanella S and Gross S 2014 Green and low temperature synthesis of nanocrystalline transition metal ferrites by simple wet chemistry routes Nano Res. 7 1027–42

[30] Tataruchuk T, Bououdina M, Vijaya J J and Kennedy L J 2016 Spinel ferrite nanoparticles: synthesis, crystal structure, properties, and perspective applications Int. Conf. on Nanotechnology and Nanomaterials (Cham: Springer) p. 305–25

[31] Bhardwaj D, Mulkherjee K and Majumder S B 2010 Wet chemical synthesis and gas sensing properties of zinc ferrite nanoparticles Mater. Chem. Phys. 120 509–17

[32] Fardood S T, Firooostan R, Moradnia A, Afshari Z and Ramazani A 2020 Green synthesis, characterization, and photocatalytic activity of cobalt chrome spinel nanoparticles Mater. Res. Express 7 015086

[33] Fardood E, Ramazani A, Fardood S T, and Gournalou F 2019 A novel green synthesis and characterization of tetragonal-spinel MgMn$_2$O$_4$ nanoparticles by tragacanth gel and studies of its photocatalytic activity for degradation of reactive blue 21 dye under visible light Mater. Res. Express 6 075057

[34] Moradnia F, Fardood S T, Ramazani A, Osali S and Abdolmaleki I 2020 Green sol–gel synthesis of CoMnCr$_2$O$_4$ spinel nanoparticles and their photocatalytic application Micro & Nano Letters 15 674–7

[35] Vinayak V, Pankaj P K, Birajdar S D, Alange R C and Jadhav K M 2015 Electrical and dielectrical properties of low-temperature-synthesized nanocrystalline Mg$_2+$substituted cobalt spinel ferrite J. Supercond. Nov. Magn. 28 3351–6

[36] Sutka A and Mezinskis G 2012 Sol-gel auto-combustion synthesis of spinel-type ferrite nanomaterials Frontiers Mater. Sci. 6 128–41

[37] Chaubal L, Shukla A K and Sreenivas K 2016 Properties of NiFe$_2$O$_4$ ceramics from powders obtained by auto-combustion synthesis with different fuels Ceram. Int. 42 12136–47

[38] Prades A, Dornier M, Djoop N and Pain-J P 2012 Coconut water uses, composition and properties: a review Fruits 67 87–107

[39] Fardood T, Saeid A R, Moradnia F, Afshari Z, Ganjikhah A and Zare F Y Green Synthesis of MgMn$_2$O$_4$ nanoparticles prepared by co-precipitation method Solid State Sci. 101–6

[40] Ateia E, Tkala E and Mohamed A T 2017 Physical and magnetic properties of Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ using XRD, magnetization and toxicity studies of ferrite particles employed as contrast agents for magnetic resonance imaging J. Magn. Magn. Mater. 363 21–5

[41] Manohar A and Krishnamoorthi C 2017 Photocatalytic study and superparamagnetic nature of Zn-doped MgFe$_2$O$_4$ colloidal size nanocrystals prepared by solvothermal reflux method J. Photochem. Photobiol., B 173 456–65

[42] Saqui H, Rahman S, Susilo R, Chen B and Dai N 2019 Structural, vibrational, electrical, and magnetic properties of mixed spinel ferrites Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanoparticles prepared by co-precipitation AIP Adv. 9 055306

[43] Alghambli N, Stroud J, Przybylski M, Zukrowski J, Hernandez A C, Brown J M, Hankiewicz J H and Celinski Z 2020 Structural, magnetic and toxicity studies of ferrite nanoparticles employed as contrast agents for magnetic resonance imaging J. Magn. Magn. Mater. 497 165981

[44] Mohammed K A, Al-Rawas A D, Gismelseed A M, Sellai A, Widallah H M, Yousef A, Elzain M E and Shongwe M 2012 Infrared and structural studies of Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrites Physica B 407 795–804

[45] Kumar D R, Ahmed S I, Lincon C A and Ravinder D 2019 Structural, optical, room-temperature and low-temperature magnetic properties of Mg$\text{Zn}$ ferronanocrystals ceramics Journal of Asian Ceramic Societies 7 53–68

[46] Tsay C-Y, Chiu Y-C and Tseng Y-K 2019 Investigation on structural, magnetic, and FMR properties for hydrothermally-synthesized magnesium-zinc ferrite nanoparticles Physica B 570 29–34

[47] Ahmed Y M Z, Ewas E M M and Zakie Z I 2010 In situ synthesis of high density magnetic ferrite spinel (MgFe$_2$O$_4$) compacts using a mixture of conventional raw materials and waste iron oxide J. Alloys Compd. 489 269–74

[48] Guinebretière R 2013 X-Ray Diffraction by Polycrystalline Materials (Hoboken, New Jersey: Wiley)

[49] Yadav S P, Shinde S S, Bhatt P, Meena S S and Rajpure K Y 2015 Distribution of cations in Co$_{1-x}$Mn$_x$Fe$_2$O$_4$ using XRD, magnetization and Mossbauer spectroscopy J. Alloys Compd. 646 550–6

[50] Moradnia F, Fardood S T, Ramazani A and Gupta V K 2020 Green synthesis of recyclable MgFeCrO$_4$ spinel nanoparticles for rapid photodegradation of direct black 122 dye J. Photochem. Photobiol., A 392 112433

[51] Fardood S, Taghavi F, Moradnia and Ramazani A 2019 Green synthesis and characterisation of ZnMn$_{2}$O$_{4}$ nanoparticles for photocatalytic photodegradation of Congo red dye and kinetic study J. Mater. Sci., Mater. Electron. 30 6741–6

[52] Denton A R and Neill W A 1991 Vegard’s law Phys. Rev. B 43 3163

[53] Wu N-L, Wang S-Y and Rusakova I A 1999 Inhibition of crystallite growth in the sol-gel synthesis of nanocrystalline metal oxides Science 285 1375–7

[54] Rane G, Koyar U, Welzel S R, Meka and Mittemeijer E J 2013 Non-monotonic lattice parameter variation with crystallite size in nanocrystalline solids Acta Mater. 61 4523–32

[55] Somvanshi S B, Mangesh V K, Khurat B P and Jadhav K M 2020 Influenal diamagnetic magnesium (Mg$^{2+}$) substitution in nano- spinel zinc ferrite ($\text{Zn}_x\text{Fe}_2\text{O}_4$): thermal, structural, spectral, optical and physiophysics analysis Ceram. Int. 46 6640–50

[56] Raut A V, Khirade P, Humbe A, Jadhav S A and Shengale D R 2016 Structural, electrical, dielectric and magnetic properties of Al$^{3+}$ substituted Ni-Zn ferrite J. Supercond. Nov. Magn. 29 1351–71
[58] Li J, Yuan H, Li G, Liu Y and Leng J 2010 Cation distribution dependence of magnetic properties of sol–gel prepared MnFe2O4 spinel ferrite nanoparticles J. Magn. Magn. Mater. 322 3396–400
[59] Reyes-Rodriguez P Y et al 2017 Structural and magnetic properties of Mg–Zn ferrites (Mg1–xZnxFe2O4) prepared by sol–gel method J. Magn. Magn. Mater. 427 268–71
[60] Raghuvanshi S, Mazaleyrat F and Kane S N 2018 Mg1–xZnxFe2O4 nanoparticles: Intercalation between cation distribution and magnetic properties AIP Adv. 8 047804
[61] Andhare D D, Supriya R P, Kousalye J S and Jadhav K M 2020 Effect of Zn doping on structural, magnetic and optical properties of cobalt ferrite nanoparticles synthesized via. Co-precipitation method Physica B 583 412051
[62] Hossain M S, Hoque S M, Liba S I and Choudhury S 2017 Effect of synthesis methods and a comparative study of structural and magnetic properties of zinc ferrite AIP Adv. 7 105321
[63] Mozaffari M, Manouchehri S, Yousefi M H and Amighian J 2010 The effect of solution temperature on crystallographic size and magnetic properties of Zn substituted Co ferrite nanoparticles J. Magn. Magn. Mater. 322 385–8
[64] Rajendran M, Pullar R C, Bhattacharya A K, Das D, Chintalapudi S N and Majumdar C K 2001 Magnetic properties of nanocrystalline CoFe2O4 powders prepared at room temperature: variation with crystallite size J. Magn. Magn. Mater. 232 71–83
[65] Chi H, Zakaria S, Yusoff M, Goh S C, Haw C Y, Ahmadi S, Huang N M and Lim H N 2010 Size and crystallinity-dependent magnetic properties of CoFe2O4 nanocrystals Ceram. Int. 36 605–9
[66] Shisode M V, Dhananjay N B, Khirade P P and Jadhav K M 2018 Structural, microstructural, magnetic, and ferroelectric properties of Ba0.5Fe1.5O4 nanocrystals Supercond. Sci. Technol. 31 2501–9
[67] Zawar S, Atiq S, Riaz S and Naseem S 2016 Correlation between particle size and magnetic characteristics of Mn-substituted ZnFe2O4 ferrites Superlattices Microstruct. 93 50–6
[68] Khirade P P, Shankar D B, Raut A V and Jadhav K M 2016 Effect of Fe–substitution on phase transformation, optical, electrical and dielectrical properties of BaTiO3 nanoceramics synthesized by sol-gel auto combustion method J. Electrocerm. 37 110–20
[69] Gul I H and Maqsood A 2008 Structural, magnetic and electrical properties of cobalt ferrite powders prepared by the sol–gel route J. Alloys Compd. 465 227–31
[70] Gul I H, Ahmed W and Maqsood A 2008 Electrical and magnetic characterization of nanocrystalline Ni–Zn ferrite synthesis by co-precipitation route J. Magn. Magn. Mater. 320 270–5
[71] Ghodake U R, Rahal C K and Suryavanshi S S 2017 Effect of Mn2+ substitution on structural, electrical transport and dielectric properties of Mg–Zn ferrites Ceram. Int. 43 1129–34
[72] Venkataramu C, Sathishkumar G and Sivakumar K 2011 Effect of Cd on the structural, magnetic and electrical properties of nanostructured Mn–Zn ferrite J. Magn. Magn. Mater. 332 1817–22
[73] Maisnam M, Phanjoubam S, Sarma H. N. K., Prakash Chandra, Devi L, Radhapiyari and Thakur. O. P. Structural and DC resistivity behaviour of Li–Mn–Ni ferrites substituted with trace amount of Co2+ Physica B 370 2005 1–5
[74] Shaikh P A, Kambale R C, Rao A V and Kolekar Y D 2009 Studies on structural and electrical properties of Co1–xNi2Fe1.9Mn0.1O4 ferrite J. Alloys Compd. 482 276–82
[75] Dionne G F and Russell G W 1987 Magnetic and dielectric properties of the spinel ferrite system Ni1−xZnxMn2−xFe2−xO4 J. Appl. Phys. 61 3868–70
[76] Raghavender A T and Jadhav K M 2009 Dielectric properties of Al-substituted Co ferrite nanoparticles Bull. Mater. Sci. 32 575–8
[77] Mansour S F and Elkestanwy M A 2011 A comparative study of electrical properties of nano–structured and bulk Mn–Mg spinel ferrite Ceram. Int. 37 1179–80
[78] Kumbhar S S, Mahadik M A, Mohite V S, Rajpure K Y, Kim J H, Moholkar A V and Bhosale C H 2014 Structural, dielectric and magnetic properties of Ni substituted zinc ferrite J. Magn. Magn. Mater. 363 114–20