# Effect of Synthesis Technique on The Structural, Electrical and Magnetic properties of zinc nanoferrite

L.C. Sonia, Maisnam Victory, Sumitra Phanjoubam

**Abstract**— Different chemical methods like sol-gel (ZS) and co-precipitation (ZC) technique have been employed to obtain zinc ferrite in the nanoregime, with an aim to study the effect of synthesis technique on their properties. The samples were sintered at 1000°C for 4 hr and were investigated for their various structural, electrical and magnetic characterizations. The lattice parameter, crystallite size, and X-ray density were calculated from the XRD data obtained. The samples synthesized by co-precipitation method were observed to have smaller crystallite size as compared to that of sol-gel prepared samples. Microstructure of the samples was recorded using scanning electron microscope (SEM) while the EDAX analysis confirmed the elemental composition of the sample. The dielectric measurements were also carried out using Agilant HP 4284A LCR meter as a function of frequency in the range 100 Hz - 1 MHz. The variation showed the normal dispersive behavior of ferrites. The magnetic properties were recorded using Vibrating Sample Magnetometer (VSM). Results obtained from the two techniques were analysed.

**Index Terms**— Co-precipitation, Dielectric, Ferrites, Sol-gel, SEM, VSM, XRD

————————————— ◆ —————————————

## 1 INTRODUCTION

MAGNETIC materials play a vital role in shaping the various development prevalent in the present society.
Of all the magnetic materials, ferrites happen to be the appropriate choice for many applications in electronics, magnetic storage, magnetic resonance imaging (MRI), magnetically controlled transfer of anti-cancer drugs, power transformers, microwave devices, detoxification of biological fluids, etc. [1], [2], [3], [4]. Nowadays, the importance of spinel-type nanoferrites having the formula $MFe_2O_4$, where M is a divalent metal ion like Ni, Co, Fe, Zn, Mn, etc. has increased notably due to its fascinating electrical and magnetic properties. The unit cell of a spinel system comprises of 8 formula units in which 32 $O^{2-}$ ions are assembled to form a face centered cubic with two non equivalent interstitial sites – tetrahedral or A sites and octahedral or B sites. A total of 64 A sites and 32 B sites are present, of which only 8A and 16 B sites are occupied by either of 8 $M^{2+}$ and 16 $Fe^{3+}$ ions. The distribution of cations at these sites determines its magnetic properties and is expressed using the formula $[M_{1-\delta}Fe_\delta]^A[M_\delta Fe_{2-\delta}]^B$ where $\delta$ defines the degree of inversion and have the value 0 for normal state and 1 for inverse state. For intermediate or partly inverted state $\delta$ lies between 0 and 1 [5], [6], [7]. The remarkable properties of $ZnFe_2O_4$ like high magnetic permeability, environment friendliness, high efficiency, high

conductivity, excellent photochemical and phase stability, small eddy current loss, low cost, etc., make it one of the most studied among the various spinel systems. The bulk $ZnFe_2O_4$ is a good example of normal spinel ferrite which behaves as an ordered antiferromagnet below 10K and exhibit paramagnetic behavior at room temperature [8], [9], [10]. Literature reveals the use of different methods for obtaining particles in the nanoregime which includes co-precipitation, combustion, ceramic, citrate precursor, sol-gel, hydrothermal, high energy ball milling, etc. [11], [12], [13], [14], [15 ].

In the present work, $ZnFe_2O_4$ nanoferrite is synthesized using sol-gel and co-precipitation method and investigations of the structural, electrical and magnetic properties were carried out using various characterization techniques.

## 2 EXPERIMENTAL

### 2.1 Synthesis methods

In sol-gel method (ZS), analytical grade iron nitrate and zinc nitrate are taken in stoichiometric proportion and dissolved in ethylene glycol in the ratio 3:1. The mixture is then heated at 40°C for about 1 hr until a clear solution is obtained. The temperature is then increased to 80°C and kept for around 20 min for gel formation. Finally, when heated at 100°C, the gel gets dried and later on gets self ignited which results in the formation of as-prepared $ZnFe_2O_4$ nanoferrite.

In co-precipitation method (ZC), appropriate amount of analytical grade ferric chloride and zinc chloride are dissolved in 150 ml of de-ionized water and heated at 40°C under constant stirring. A precise control of the pH to 11 is made through dropwise addition of sodium hydroxide, which serves as the precipitating agent. The obtained brown colored precipitate is filtered and washed several times using de-

————————————————
- **L.C. Sonia**
  *M.Sc Physics, Manipur University, India,*
  *PH-8258021850, E-mail: laishangbamsonia@gmail.com*
- **Maisnam Victory**
  *Research Scholar, Physics Department, Manipur University*
  *E-mail: victory.mais@gmail.com*
- **Sumitra Phanjoubam**
  *Professor*
  *Dept. of Physics, Manipur University*
  *E-mail: sumitraphanjoubam@gmail.com*

ionized water until its pH becomes neutral and then dried.

The as-prepared samples are pre-sintered at 750°C for 2 hr. The powder is then mixed with 3% wt. of polyvinyl alcohol which acts as binder and pressed into pellet with 100 Kg/cm² pressure using a hydraulic press. Final sintering of the pellet sample is done at 1000°C for 4 hr and then furnace cooled in air at room temperature.

## 2.2 Characterization tools

The structural investigation of the as-prepared and annealed samples are carried out using Phillips X'Pert Pro Panalytic X-ray Diffractometer with CuKα radiation of wavelength λ=1.5406 Å, and variation of the scanning angle (2θ) in the range 20 to 80 degrees. The photomicrographs taken from SEM FEI QUANTA-250 are used for analyzing the morphology and microstructure of the samples while the EDAX analysis confirms the elemental composition. The electrical and magnetic properties are investigated using Agilant HP 4284A LCR meter and Vibrating Sample Magnetometer (VSM).

## 3 RESULTS AND DISCUSSION

Fig. 3.1 and Fig. 3.2 shows the XRD pattern of the as-prepared and annealed ZS and ZC samples respectively. The pattern matches with the standard ICSD card No. 01-070-6393 and confirm the single phase spinel structure without any extra peaks. The desired peaks are indexed as (220), (311), (222), (400), (422), (511) and (440). The observed peaks of the as-prepared samples are less intense and broadened, indicating initial phase in the formation of the polycrystalline $ZnFe_2O_4$ associated with high degree amorphous phases. However, with annealing, the intensity increases immensely and broadening decreases appreciably signifying inclusion of more crystalline phases and increase in crystallite size.
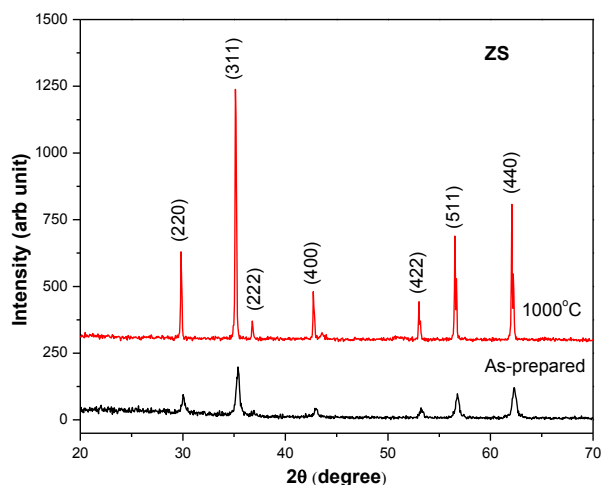


Fig. 3.1 XRD pattern of the as-prepared and annealed ZS sample

As the sample crystallizes in fcc arrangement the lattice constant, a, is calculated using the relation,
$d_{hkl} = a / (h^2+k^2+l^2)^{1/2}$ , where h, k, l are the Miller indices and

the $d_{hkl}$ gives the inter-planar spacing which defines the dimensions of the unit cell. The crystallite size is calculated using Scherrer's formula taking into account the β value (full width at half maximum) of the most intense (311) diffraction peak [2], [ 3]. The structural parameters calculated using the data generated from X-ray analysis are recorded in Table 1.
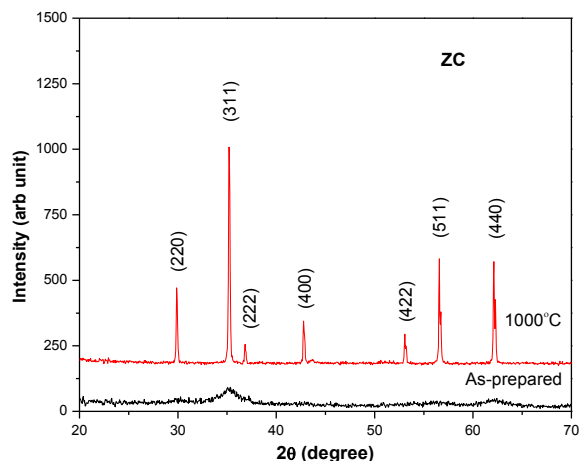


Fig. 3.2 XRD pattern of the as-prepared and annealed ZC sample

**Table 1: Record of the lattice constant (a), crystallite size (D), densities and porosity (P)**

| Sample | a (Å) | D (nm) | $d_{th}$ (g/cm³) | $d_{exp}$ (g/cm³) | P % |
|---|---|---|---|---|---|
| ZS | 8.419 | 22 | 5.337 | - | |
| ZS at 1000°C | 8.458 | 85 | 5.264 | 4.123 | 21.68 |
| ZC | 8.448 | 3.8 | 5.283 | - | |
| ZC at 1000°C | 8.449 | 75 | 5.281 | 3.376 | 36.07 |

Table1 clearly indicates the value of the lattice parameter to be in good agreement with the lattice parameter of the normal spinel $ZnFe_2O_4$ (~8.4412 Å) [16]. The crystallite size of the synthesized sample is found to be well within the desired nanorange (1-100 nm). It is also found that the ZC sample yields smaller crystallite size than the ZS sample. The theoretical or X-ray density is calculated applying the relation, $d_{th} = 8M/(N_A a^3)$, where M is the molecular weight of $ZnFe_2O_4$ and $N_A$ is the Avogadro's number. The experimental densities are also obtained by taking the ratio of weight to its corresponding volume. The higher experimental density of ZS as compared to ZC sample annealed at the same temperature may be related to its lower porosity.

Fig. 3.3 depicts the SEM photomicrographs of the as-prepared ZS and ZC indicating possible agglomeration of the finer grains. SEM photomicrographs of the annealed ZS and ZC samples recorded on a fractured piece of pellets are shown

in Fig. 3.4. The average grain size of the annealed ZS and ZC samples are found to be 215 nm and 195 nm respectively. The morphological study indicates voids and pores as seen in the SEM image of the annealed ZS sample, and can probably be correlated to the outward release of gas during self ignition process [4]. It is also seen from the SEM photomicrograph that the ZS samples are more spherical in shape and homogenously distributed as compared to ZC samples.
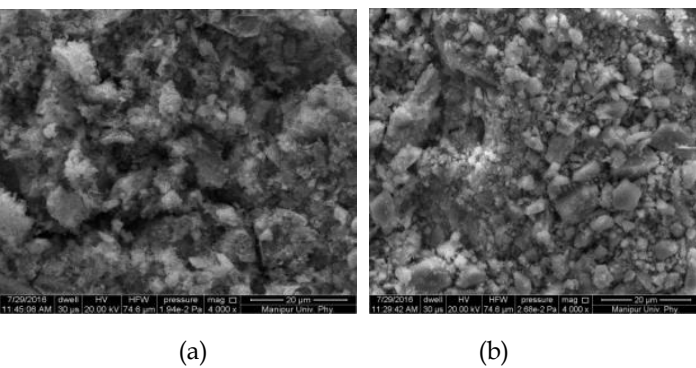


(a)                              (b)
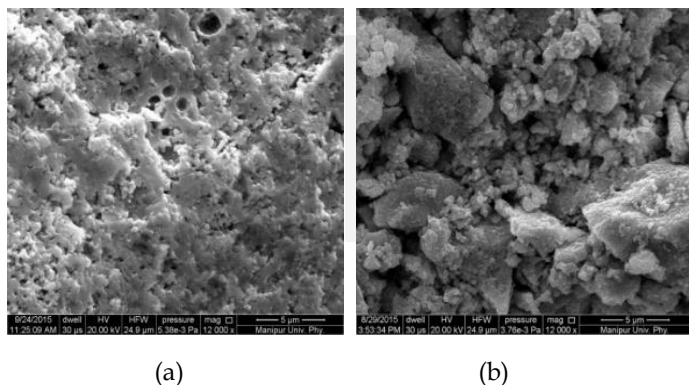
Fig. 3.3 SEM images of as-prepared (a) ZS and (b) ZC sample.



(a)                              (b)

Fig. 3.4 SEM images of annealed (a) ZS and (b) ZC sample

**Table 2: Elemental percentage content of $ZnFe_2O_4$ samples**

| Sample | Zn | Fe | O |
|---|---|---|---|
| ZS | 24.58 | 52.72 | 22.70 |
| ZS at 1000°C | 14.16 | 32.57 | 53.27 |
| ZC | 19.95 | 47.96 | 32.09 |
| ZC at 1000°C | 14.67 | 32.68 | 52.65 |

The atomic abundance of the elements Zn, Fe and O is provided by the energy dispersive X-ray (EDAX) analysis using the detector SDD Apollo X embedded in the SEM FEI QUANTA-250 operated at 20 keV. The relevant percentage content of the various elements is given in Table 2. It is evident from the data that the ZS and ZC sample annealed at 1000°C preserves the desired stoichiometric proportions. Fig. 3.5 represents the EDAX spectrum of the as-prepared and annealed ZS and ZC samples giving a vivid scenario of the elements present with nonexistence of impurity [4], [5].

The frequency dependence of dielectric constant and dielectric loss are recorded on pellets of ZS and ZC samples annealed at 1000°C using Agilant HP 4284A LCR meter in the frequency range 100 KHz to 1 MHz and is depicted in Fig. 3.6. This study confirmed the normal dispersive behavior of ferrites.
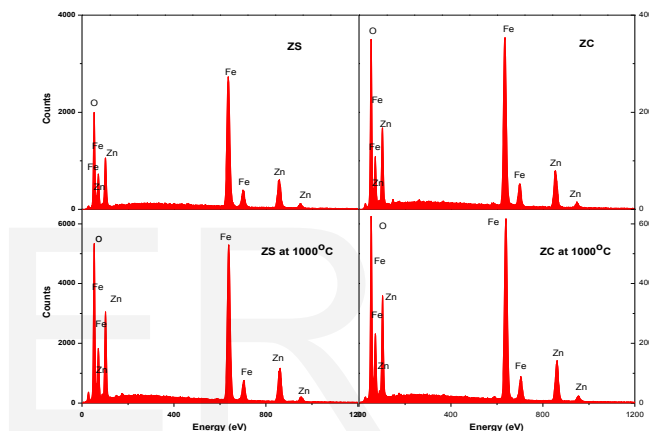


Fig. 3.5 EDAX spectrum of the $ZnFe_2O_4$ nanoferrite
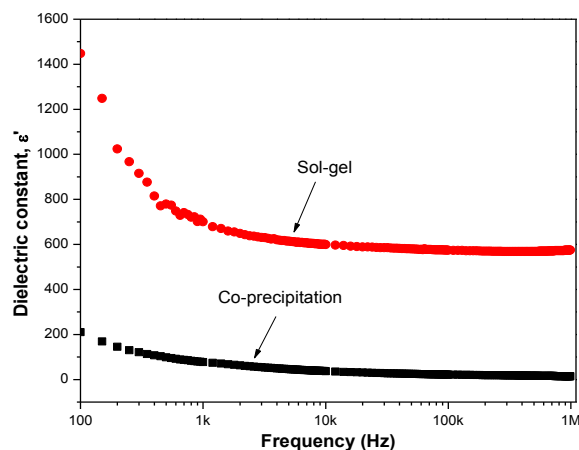


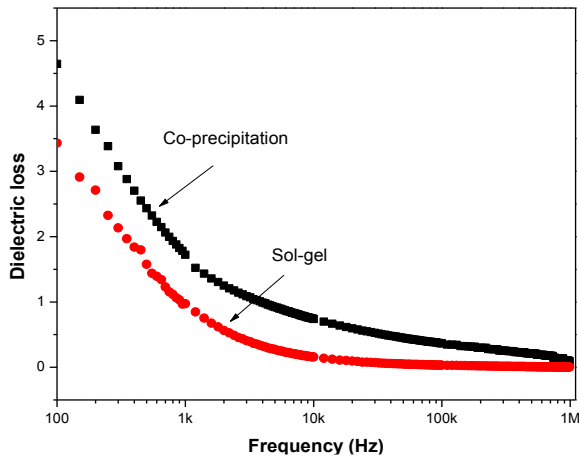Fig. 3.6 Variation of dielectric constant with frequency

Fig. 3.7 Variation of dielectric loss with frequency.

High value of the dielectric constant is observed at lower frequency which decreases abruptly with increase in frequency. As the frequency is further increased the dielectric constant reduces to a low value and becomes nearly constant. The obtained dispersive nature of the ferrites may be explained using Koops two layer model and conduction mechanism which connects with the space charge polarization [17], [18], [19]. As known, ferrites are composed of conducting grains which are separated by non-conducting grain boundaries. Their conduction mechanism is governed by the electron hopping between the ions of different valency located at crystallographic equivalent sites and is popularly known as the Verwey mechanism of electron hopping [20]. The electron hopping in $ZnFe_2O_4$ takes place between the $Fe^{2+}$ ions formed during sintering and the $Fe^{3+}$ ions at the B-sites since the $Fe^{2+}$ ions have preference for B-sites. The non-conductive grain boundaries offer high resistance thereby blocking the mobile charge carriers displaced in accordance with the direction of the applied field. The hinderance in charge migration leads to collection of space charge carriers at the boundary causing polarization in the low frequency region. With increase in frequency, the direction reversal of electron motion increases thereby, decreasing the probability of electrons reaching the grain boundary and hence the observed decrease in the dielectric constant. The almost constant low value of dielectric constant at much higher frequency may be due to inability of the electron hopping to follow the frequencies of the applied field [21], [22], [23].

As seen from Fig. 3.7 the dielectric loss decreases continuously in the frequency range under investigation. The observed trend may be understood from the relation $tan\delta=1/\omega\epsilon'\rho$, where angle $\delta$ is the lag in phase by the induced current from the applied field, $\omega$ gives the angular frequency and $\rho$ is the resistivity of the sample under investigation. The observed dielectric loss may due to various process like decrease in polarization contributed by grain boundaries, crystal imperfections and presence of impurities. The porosity of the sample which depends on the density factor may also

contribute to the observed trend. The higher porosity of the annealed ZC sample in comparision with ZS sample implies low denseness resulting in lower dielectric constant and higher dielectric loss [24], [25].

The M-H loop for the samples are given in Fig. 3.8 and the values of saturation magnetization ($M_s$), coercivity ($H_c$) and remanent magnetization ($M_r$) are recorded in Table 3. Higher magnetization observed for ZS samples may be attributed to larger crystal size (Table 1), as crystalline nature has profound impact on the magnetization property of ferrite. The magnetization value for both the samples decrease with annealing. This observed decrease may be due to partial inversion arising out of relocation of iron and zinc ions between the two non-equivalent interstitial sites [10], [11], [12].

The coercive force in polycrystalline ferrites is known to influence by various factors like anisotropy, porosity, particle size, etc. It is observed from Fig. 3.9 that the coercivity for the as-prepared samples increases with increase in particle size and then reaches a maximum and then decreases for the annealed samples with further increase in particle size thereby indicating the change in domain nature from single domain region to multi-domain region [26].
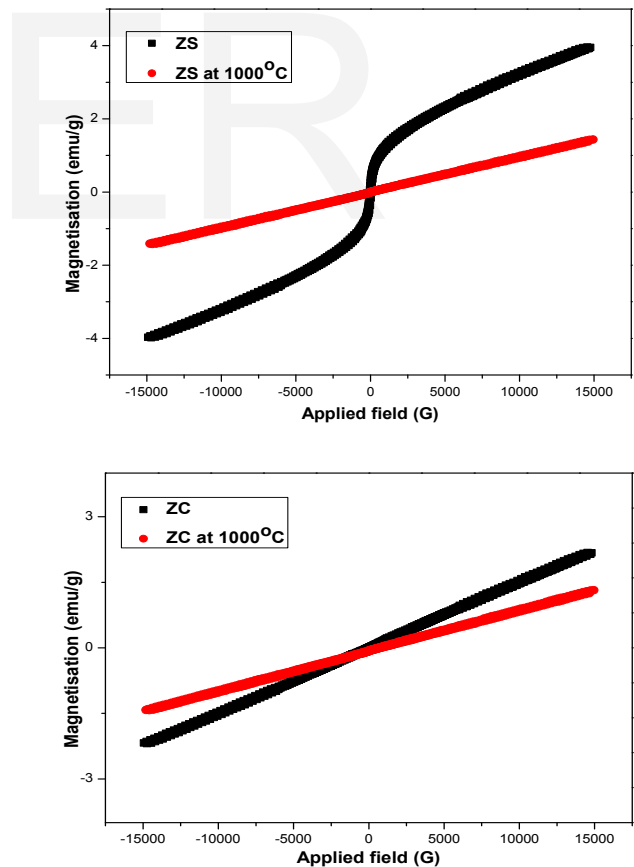




Fig. 3.8 M-H loop for the $ZnFe_2O_4$ samples.

**Table 3: Magnetic data for as-prepared and annealed ZnFe$_2$O$_4$ nanoferrite**

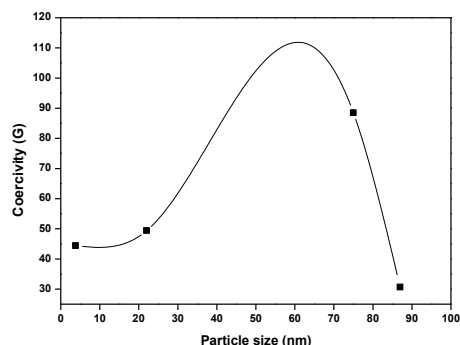|  | $M_s$(emu/g) | $H_c$ (G) | $M_r$(emu/g) |
|---|---|---|---|
| **ZS** | 3.97 | 49.41 | 0.0078 |
| **ZS at 1000°C** | 1.4259 | 30.675 | 0.0045 |
| **ZC** | 2.19 | 44.38 | 0.2727 |
| **ZC at 1000°C** | 1.3725 | 88.497 | 0.0082 |



Figure 3.9: Variation of coercivity (H$_c$) with particle size (D)

## 4. CONCLUSIONS

In the present communication, preparation of ZnFe$_2$O$_4$ nanoferrite is being conducted successfully using two chemical methods i.e. sol-gel and co-precipitation method. Various structural, microstructural, electrical and magnetic studies are performed. XRD pattern confirmed the spinel phase of the as-prepared and annealed samples and structural parameters are calculated using the data obtained. Morphological studies of the sample is carried out using SEM technique and EDAX analysis gives the elemental composition which are found to be in stoichiometric proportions with absence of impurity phase. The ZS sample is found to possess higher dielectric constant with lower dielectric loss tangent value as compared to ZC sample and thus proves attractive for various electrical studies. Magnetic properties are studied using VSM measurement and the variation of coercive force with particle size indicates the change in domain nature from single domain to multi-domain region.

## ACKNOWLEDGMENT

## REFERENCES

[1] J. Mayekar and V. Dhar, S.Radha, "Synthesis, Characterisation and Magnetic Study of Zinc Ferrite Nanoparticles," *Int. J. Innovative Research in Science, Engineering and Technology*, vol. 5, issue 5, May 2016, doi:10.15680/IJIRSET.2016.0505268.

[2] S. Deka and P.A. Joy, "Characterization of nanosized NiZn ferrite powders synt hesized by an autocombustion method," *Materials Chemistry and Physics*, vol. 100, pp. 98-101, 2006, doi: 10.1016/j.matchemphys.2005.12.2012.

[3] M.A. Ahmad, H.H. Afify, I.K. El Zawawia and A.A. Azab, "Novel structural and magnetic properties of Mg doped copper nanoferrites prepared by conventional and wet methods," *J. Magn. Magn. Mater.*, vol. 324, pp. 2199-2204, 2012, doi: 10.1016/jmmm.2012.02.025.

[4] N.M. Deraz and A. Alarfi, "Microstructure and Magnetic Studies of Zinc Ferrite Nanoparticles," *Int. J. Electrochem. Sci.*, vol. 7, pp. 6501-6511, 2012.

[5] Binu P Jacob, Ashok Kumar, R P Pant, Sukhvir Singh and E M Mohammed, "Influence of preparation method on structural and magnetic properties of nickel ferrite nanoparticles," *Bull. Mater. Sci.*, vol. 34, no. 7, pp. 1345-1350, December 2011.

[6] K. Praveena and K. Sadhana, "Ferromagnetic Properties of Zn substituted Spinel Ferrites for High Frequency Applications," *International Journal of Scientific and Research Publications*, vol. 5, no. 4, April 2015.

[7] Marykutty Thomas and K C George, "Infrared and magnetic study of nanophase zinc ferrite," *Indian Journal of Pure & Applied Physics*, vol. 47, pp. 81-86, February 2009.

[8] P. Sivagurunathan and K. Sathiyamurthi, "Effect of Temperatures on Structural, Morphological and Magnetic Properties of Zinc Ferrite Nanoparticles," *Canadian Chemical Transactions*, vol. 4, no. 2, pp. 244-254, 2016, doi: 10.13179/canchemtrans.2016.04.02.0299.

[9] Mohammad Niyaifar, "Effect of Preparation on Structure and Magnetic Properties of ZnFe$_2$O$_4$," *Journal of Magnetics*, vol. 19, no. 2, pp. 101-105, 2014, doi: 10.4283/JMAG.2014.19.2.101.

[10] C N Chinnasamy, A Narayanasamy, N Ponpandian, K Chattopadhyay, H Guérault and J-M Greneche, "Magnetic properties of nanostructured ferromagnetic zinc ferrite," *J.Phys.: Condens. Matter*, vol. 12, pp. 7795-7805, 2000.

[11] T.F. Marinca, I. Chicinas, O. Isnard and V. Pop, "Structural and magnetic properties of nanocrystalline ZnFe$_2$O$_4$ powder synthesized by reactive ball milling," *Optoelectronics and Advanced Materials – Rapid Communications*, vol. 5, no. 1, pp. 39-43, January 2008.

[12] Ashok kumar, Parmod Kumar, Geeta Rana, M. S.Yadav and R. P. Pant, "A study on structural and magnetic properties of Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ (0 ≤ x ≤ 0.6) ferrite nanoparticles," *Applied Science Letters*, vol. 1, no. 2, pp. 33-36, April 2015, doi: 10.17571/appslett.2015.01009.

[13] Amarjeet and Vinod Kumar, "Synthesis, Thermal and FTIR Study of Zn-Fe Nano Ferrites," *International Journal of Latest Research in Science and Technology*, vol. 3, no. 1, pp. 61-63, Jan/Feb 2014.

[14] Abdalrawf I. Ahmed, Mohamed A. Siddig, Abdulmajid A. Mirghni, Mohamed I. Omer and Abdelrahman A. Elbadawi, "Structural and Optical Properties of Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ Nano-Ferrites Synthesized Using Co-Precipitation Method," *Advances in Nanoparticles*, vol. 4, pp. 45-52, 2015, doi: 10.4236/anp.2015.42006.

[15] Chandrashekhar A. Ladole, "Preparation and Characterization of Spinel Zinc Ferrite ZnFe$_2$O$_4$," *Int. J. Chem. Sci.*, vol. 10, no. 3, pp. 1230-1234, 2012.

[16] R. Raeisi Shahraki, M. Ebrahimi, S.A. Seyyed Ebrahimi and S.M. Masoudpanah, "Structural characterization and magnetic properties of superparamagnetic zinc ferrite nanoparticles synthesized by the coprecipitation method," *J. Magn. Magn. Mater.,* vol. 324, pp. 3762-3765, 2012, doi: 10.1016/j.jmmm.2012.06.020.

[17] C. G. Koops, "On the Dispersion of Resistivity and Dielectric Constant of Some Semiconductors at Audiofrequencies," *Physical Review*, vol. 83, no. 1, July 1951.

[18] J.C Maxwell, *Electricity and Magnetism*, Oxford University Press, London, vol. 1, sec 328, pp. 376, 1873.

[19] K.W. Wagner, *Ann. Phys.*, vol. 40, pp. 817, 1913.

[20] E.J.W. Verwey and P.W. Haayman, "Electronic Conductivity and Transition Point of Magnetite ('$Fe_3O_4$')," *Physica*, vol. 8, no. 9, pp. 979-987, 1941, doi: 10.1016/S0031-8914(41)80005-6.

[21] K. Rama Krishna, Dachepalli Ravinder, K.Vijaya Kumar, Utpal S. Joshi and V. A. Rana, "Dielectric Properties of Ni-Zn Ferrites Synthesized by Citrate Gel Method," *World J. of Condensed Matter Physics*, vol. 2, pp. 57-60, May 2012, doi: 10.4236/wjcmp.2012.22010.

[22] P. U. Mahamuni and B.K. Chougule, "Structural, Dielectric and Magnetic Properties of Nanocrystalline Ni-Zn Ferrites," *Archives of Physics Research*, vol. 1, no. 1, pp. 112-118, 2010.

[23] Anshu Sharma, Kusum Parmar, R.K. Kotnala, N.S. Negi, "Magnetic and Dielectric Properties of $Co_xZn_{1-x}Fe_2O_4$ Synthesized by Metallo – Organic Decomposition Technique," *Int. J. Advances in Engineering and Technology*, vol. 5, pp. 544-554, Nov. 2012.

[24] Amarendra K. Singh, A. Verma, O.P. Thakur, Chandra Prakash, T.C. Goel and R.G. Mendiratta, "Electrical and magnetic properties of Mn-Ni-Zn ferrites processed by citrate precursor method," *Materials Letters*, vol. 57, pp. 1040-1044, Jan 2003.

[25] Md. T. Rahman, M. Vargas and C.V. Ramana, "Structural characteristics, electrical conduction and dielectric properties of gadolinium substituted cobalt ferrite," *Journal of Alloys and Compounds*, vol. 617, pp. 547-562, August 2014, doi: 10.1016/j.jallcom.2014.07.182.

[26] B.D. Cullity, C.D. Graham, *Introduction to Magnetic materials*. IEEE Press, John Wiley & Sons, New Jersey, pp. 360-361, 2009.