Structural and dielectric properties of mixed spinel ferrite Cu(0.7)Zn(0.3)Fe₂O₄ nanoparticles

S B Kale¹, R M Borade², J S Kounsalye³ A V Raut¹, S R Nimbhore³ and K M Jadhav⁴

¹Department of Applied Sciences, Government Polytechnic College, Aurangabad 431004
²Department of Chemistry, The Institute of Science, Dr Homi Bhabha State University, Mumbai 400032
³Department of Physics, Late. R. B. Arts, Commerce and Smt. S. R. B. Science College, Arni, Dist. Yavatmal, India (MS)
⁴Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431004 India

Corresponding author email: drjadhavkm@gmail.com

Abstract. In this communication we report structural and dielectric properties of mixed Cu-Zn spinel ferrite nanoparticles. Cu₀.₇Zn₀.₃Fe₂O₄ nanoparticles were synthesized by using standard and well known sol-gel auto-combustion techniques. The obtained nanoparticles were annealed at 520°C for 4 h and then used for further study. The X-ray diffraction (XRD) pattern was recorded at room temperature to investigate the single phase nanocrystalline nature of prepared sample. The XRD pattern shows formation of single phase cubic spinel structure with average crystallite size of ~24 nm. The crystallite size was determined by using standard Scherrer’s equation. The other structural parameters like lattice constant, unit cell volume, X-ray density etc. were determined using XRD data. The dielectric properties were measured at room temperature and as a function of frequency using LCR-Q meter. The dielectric constant, dielectric loss and dielectric loss tangent all get decreased exponentially with increasing frequencies. The observed dielectric behaviour is similar to that of reported in the literature.

1. Introduction

Ferrites with iron oxide and metal oxide as a constituent magnetic materials are used in several technological applications [1]. They exhibit both kinds of properties that are ferromagnetic and electrical. They possess high electrical resistivity [2], low eddy current and dielectric loss, magnetization, high Curie temperature and therefore ferrites are known to be good magnetic and dielectric materials [3]. On account of their important electrical, dielectric and magnetic properties they are used in microwave devices [4, 5] high frequency applications, antenna rods [6, 7], memory
storage devices [8, 9] etc. These materials are continuously studied from last 7-8 decades because of their excellent twin properties of electrical insulator and magnetic conductor which can be improved by several ways. One of the important parameter for generating variations in the physical properties of the ferrite is the selection of synthesis method. Earlier, Ferrites were synthesized by ceramic technique [10], it has some inherent drawbacks. Some of the drawbacks are it requires high temperature, extended synthesis time and lack of technological approach. The drawbacks of ceramic method are overcome with the help of wet chemical synthesis method. Some of the wet chemical methods are sol-gel method [11, 12], sol-gel auto-combustion, co-precipitation [13, 14], micro-emulsion [15], hydrothermal [16] etc. All the wet chemical methods are advantages over the conventional ceramic method as they required low temperature for synthesis; the method yields high quality homogeneous powder. This method is simple and cost effective [17, 18], also this method requires least time as compared to the conventional ceramic method. This wet chemical method has gained an importance in the recent years. In this work, we have used the sol-gel auto combustion method for the synthesis of mixed \( \text{Cu}_{(0.7)}\text{Zn}_{(0.3)}\text{Fe}_2\text{O}_4 \) (CZK_7). Spinel ferrite with the chemical formula \( \text{MF}_2\text{O}_4 \) \((\text{M} = \text{divalent cations like Cu, Zn, Co, Mn, Fe etc.})\) have cubic spinel structure with a space group \( \text{Fd}_{\text{im}} \) [19, 20]. The spinel ferrite possesses two interstitial sites namely tetrahedral (A) and octahedral (B), in which contains of different valence and size can accommodate at appropriate site. Copper ferrite is a unique spinel ferrite and has tetragonal as well as cubic spinel structure dependently on the synthesis methods and conditions. Zinc (\( \text{Zn}^{2+} \)) is a divalent nonmagnetic cation can easily be incorporated in the lattice of copper ferrite. Thus, the mixed Cu-Zn spinel ferrite with the formula \( \text{Cu}_{(0.7)}\text{Zn}_{(0.3)}\text{Fe}_2\text{O}_4 \) (CZK_7) was prepared in the present study by well-known wet chemical method. The structural and dielectric properties were investigated by means of X-Ray diffraction and LCR-Q meter. The applied characterization techniques, structural and dielectric properties of \( \text{Cu}_{(0.7)}\text{Zn}_{(0.3)}\text{Fe}_2\text{O}_4 \) (CZK_7) ferrite nanoparticles are reported in this communication.

2. Experimental

2.1 Raw Materials

\( \text{Cu}_{(0.7)}\text{Zn}_{(0.3)}\text{Fe}_2\text{O}_4 \) (CZK_7) spinel ferrite nanoparticles have been prepared by sol-gel auto-combustion method in order to achieve homogeneous crystal structure. A stoichiometric proportion of metal nitrate solutions were used as a synthesis protocol. The purity, chemical strength and brand trust of these materials were checked for the laboratory synthesis of \( \text{Cu}_{(0.7)}\text{Zn}_{(0.3)}\text{Fe}_2\text{O}_4 \) (CZK_7) spinel ferrite nanoparticles. 99.9% pure AR graded ferric nitrate \((\text{Fe(NO}_3)_3\cdot9\text{H}_2\text{O})\) [21], copper nitrate \((\text{Cu(NO}_3)_2)\) [22] and zinc nitrate \((\text{Zn(NO}_3)_2)\) [23] was taken as a starting material for the present synthesis. Fuel plays an important role in sol-gel auto-combustion method, so we used citric acid \((\text{C}_6\text{H}_8\text{O}_7)\) [24] as a fuel due to its wonderful complexing ability. Citric acid also has a low ignition temperature (200°C - 250°C) than that of the other fuels used in wet chemical methods.

2.2 Synthesis Method

Beginning with the starting materials, metal nitrate to citric acid ratio was taken as 1:3 for the synthesis of \( \text{Cu}_{(0.7)}\text{Zn}_{(0.3)}\text{Fe}_2\text{O}_4 \) (CZK_7) spinel ferrite nanoparticles. The metal nitrates were stirred well with a drop by drop addition of liquid ammonium hydroxide \((\text{NH}_4\text{OH})\). An addition of ammonium hydroxide in metal nitrates helps to maintain the pH of the solution at 8. The mixed metal nitrate solution was stirred continuously and heated at 75 °C on a hot plate magnetic stirrer for 4 to 5 h. This step would helpful for the formation of sol in the reaction. Under the constant stirring and heating a transparent sol was heated at 100 °C for 1.5 h. On removal of water at some extend, small increase in temperature leads the reaction from transparent sol to a viscous brown gel. This viscous brown gel further transformed into a dried gel. Further, nitrate-citrate gel reaction takes place to dried gel formation which exhibited self-propagating combustion behaviour. At a particular temperature
ignition started and dry gel burnt in self-propagating combustion manner. The gel was burnt out completely and forms a loose powder of Cu_{0.7}Zn_{0.3}Fe_{2}O_{4} (CZK_7) spinel ferrite. The obtained nanoparticles were annulated at 520°C for 4 h and then used for the further characterization.

3. Characterization

3.1 X-Ray Diffraction

The X-ray diffraction study of prepared Cu_{0.7}Zn_{0.3}Fe_{2}O_{4} (CZK_7) spinel ferrite nanoparticles was performed on a Philips PW-1730 X-ray diffraction using Cu-ka radiation (λ = 1.5405 Å). The X-ray diffraction pattern was recorded in the 2θ range of 20°-80° at room temperature. Using XRD data various structural parameters were obtained.

3.2 Dielectric Properties

Dielectric properties of spinel ferrites are important because of their use in microwave applications. In the present study, dielectric properties of Cu_{0.7}Zn_{0.3}Fe_{2}O_{4} (CZK_7) are studied by means of LCR-Q meter (Model HP 4284 A) as a function of frequency and at room temperature.

4. Results and discussion

4.1 Structural Properties

Figure 1 represents the room temperature XRD pattern of the Cu_{0.7}Zn_{0.3}Fe_{2}O_{4} (CZK_7) sample. The reflections were identified as (111), (220), (311), (222), (400), (422), (511) and (400). These reflections were oriented at 2θ angles 18.218°, 30.057°, 35.418°, 38.669°, 43.101°, 53.442°, 56.942° and 62.506 angles respectively which reveals cubic spinel structure of Cu_{0.7}Zn_{0.3}Fe_{2}O_{4} (CZK_7) [25]. These XRD has characteristics peaks matching with JCPDS card number PDF#340425. The values of Bragg's angle interplanar space and corresponding Miller Indices are given in the table 1.

![Figure 1. X-ray Diffraction pattern of Cu_{0.7}Zn_{0.3}Fe_{2}O_{4} (CZK_7) spinel ferrite nanoparticles](image-url)

The analysis of XRD data reveals that the prepared samples belongs to cubic spinel structure and is nanocrystalline in nature. The XRD data was used to evaluate various structural parameters like lattice constant, X-ray density etc..

The lattice constant of Cu(0.7)Zn(0.3)Fe2O4 (CZK_7) spinel ferrite nanoparticles was calculated from the formula [26]:

\[ a = d_{hkl} \left( h^2 + k^2 + l^2 \right)^{\frac{1}{2}} \]  

(1)

Where, \( d \) is interplanner spacing, \( hkl \) are the Miller indices and \( a \) is lattice constant. From the XRD data (FWHM of strongest Bragg’s reflection (311) oriented at 2\( \theta = 35.418^\circ \)) was considered to calculate crystallite size (t) using Scherrer’s formula [27]:

\[ t = \frac{k\lambda}{\beta \cos \theta} \]  

(2)

Where, \( K \) is a shape factor = 0.9, \( \lambda = 1.5405 \) Å, \( \theta \) is the Bragg’s diffraction angle and \( \beta \) is the FWHM of the broadening of diffraction line (in radian).

**Table 1.** Bragg’s angle (2\( \theta \)), Sin\( \theta \), interplanar space (d), Miller Indices (hkl) and lattice constant (a)

| (hkl) | 2\( \theta \) | \( \theta \) | sin\( \theta \) | \( d_X \) (\( g/cm^2 \)) | \( a \) (Å) |
|-------|-------------|-------------|----------------|-----------------|-------------|
| (111) | 18.218      | 9.109       | 0.1583         | 4.8656          | 8.4274      |
| (220) | 30.057      | 15.0285     | 0.2707         | 2.9706          | 8.9355      |
| (311) | 35.418      | 17.709      | 0.3041         | 2.5323          | 8.3890      |
| (222) | 38.669      | 19.3345     | 0.3310         | 2.3266          | 8.0595      |
| (400) | 43.101      | 21.5505     | 0.3673         | 2.0970          | 8.3880      |
| (422) | 53.442      | 26.721      | 0.4496         | 1.7131          | 8.3924      |
| (511) | 56.942      | 28.471      | 0.4767         | 1.6158          | 8.3959      |
| (440) | 62.506      | 31.253      | 0.5188         | 1.4847          | 8.3987      |

The X-ray density of Cu(0.7)Zn(0.3)Fe2O4 (CZK_7) ferrite nanoparticles was calculated by:

\[ d_x = \frac{8M}{Na^3} \]  

(3)

Here 8 is a number of molecules for unit cell of spinel lattice, M is a Molecular weight in gram mole of the spinel and N = Avogadro number. The values of lattice constant, unit cell volume, X-ray density, and crystallite size were listed in table 2.

**Table 2.** Values of lattice constant (a), unit cell volume (V), X-ray density (dx), crystallite size (t).

| \( a \) (Å) | \( V \) (Å³) | \( d_X \) (\( g/cm^3 \)) | \( t \) (nm) |
|-------------|-------------|-----------------|-------------|
| 8.422       | 597.53      | 5.330           | 24.17       |

It is evident from table 2 that, the lattice constant was found to be increased when zinc is doped in copper ferrite. The increase in lattice constant can be attributed to the larger ionic radius of Zn\(^{2+}\) ion (0.082 nm) which replaces a smaller Fe\(^{3+}\) ion (0.067 nm) [28]. The value of crystallite size (t) indicates the nanocrystalline nature of the prepared samples. Our results on lattice constant and other structural parameters are in a good agreement with the reported values [15].

4.2 Dielectric properties

The dielectric properties are studied by means of LCR Q meter and as a function of frequency at room temperature. The dielectric behavior of Cu(0.7)Zn(0.3)Fe2O4 (CZK_7) ferrite nanoparticles can be
explained on the basis of Maxwell-Wagner interfacial polarization which is in agreement with Koop’s phenomenological theory. CuFeO$_4$ is an inverse spinel structure [29] with Cu$^{2+}$ ions occupying octahedral [B] site by replacing Fe$^{3+}$ ions which results in decrease in Fe$^{3+}$ ions at octahedral [B] site.

In the present study, the dielectric constant, dielectric loss and dielectric loss tangent were calculated using standard relations reported in the literature and their variation with respect to frequency was studied. The measurements of the dielectric properties were recorded from 100 Hz- 1 MHz. By measuring capacitance C, the dielectric parameters were calculated.

![Graph of dielectric constant vs. frequency](image)

**Figure 2.** Dielectric constant ($\varepsilon'$) of Cu$_{(0.7)}$Zn$_{(0.3)}$Fe$_2$O$_4$ (CZK_7) spinel ferrite nanoparticles

### 4.2.1 Dielectric constant ($\varepsilon'$)

Figure 2 represents the variation of dielectric constant ($\varepsilon'$) as a function of frequency. The plot shows exponential nature. At low frequencies, the dielectric constant is maximum and at higher frequencies, dielectric constant is minimum. This type of behaviour of dielectric constant was repeated in various spinel ferrite nanoparticles [30]. The observed decrease in dielectric constant with increase in frequency can be explained as at higher frequency any effect contributing a polarization is found to show lagging behind the applied field when frequency is increased beyond a certain frequency limit, the electron hopping cannot follow the electric field fluctuation and causes decreasing dielectric constant. These types of polarization are due to the inhomogeneous dielectric structure, like porosity and grain boundaries in the samples.

### 4.2.2 Dielectric loss ($\varepsilon''$)

Figure 3 represents the variation of dielectric loss as a function of frequency. The dielectric loss ($\varepsilon''$) decreases with increase in frequency as observed for dielectric constant ($\varepsilon'$).
Figure 3. Dielectric loss ($\varepsilon''$) of Cu$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ (CZK$_7$) spinel ferrite nanoparticles

At lower frequency the dielectric loss is maximum and at higher frequency the dielectric loss was recorded to be minimum which can be seen in figure 3.

4.2.3 Dielectric loss tangent ($\delta$)

Figure 4 represents the frequency dependent dielectric loss tangent ($\tan \delta$) plot for mixed Cu$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ (CZK$_7$) ferrite nanoparticles. Dielectric loss tangent plot exhibits similar nature as that of the dielectric constant ($\varepsilon'$).

Figure 4. Dielectric loss tangent ($\delta$) of Cu$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ (CZK$_7$) spinel ferrite nanoparticles

Here, the dielectric loss tangent ($\delta$) decreases with increase in frequency. At higher frequencies the dielectric loss tangent is minimum and at low frequencies the dielectric loss tangent ($\delta$) was found to be maximum.
5. Conclusions

The mixed Cu$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ (CZK$_7$) spinel ferrite nanoparticles have been successfully prepared by wet chemical sol-gel auto-combustion method. It was evident from XRD pattern that Bragg’s angle ($2\theta$) reflections are in very good agreement with the reported literature confirming the cubic spinel structure of (CZK$_7$). The Lattice constant (a) ~8.422 Å and other structural properties are in the reported range. The crystallite size (t) of the CZK$_7$ nanoparticles was measured ~24.17 nm which is a good achievement from the synthesis point of view for the present investigation. The dielectric constant ($\varepsilon'$) decreases to a minimum value of frequency range (Hz) and remains almost constant for higher frequency range. Initially, the dielectric loss ($\varepsilon''$) was maximum and found to be decreases with increasing frequency. The dielectric loss tangent ($\delta$) plot exhibits similar nature as that of the dielectric constant ($\varepsilon'$) which decreases exponentially as a function of frequency. Considering the technological demands of the ferrite nanoparticles, overall investigation leads to a conclusion that the structural and dielectric study of Cu$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ (CZK$_7$) spinel ferrite nanoparticles can be useful for high frequency applications.

Acknowledgement

One of the author S B Kale is thankful to Dr S M Patange, Department of Physics, Shrikrishna Mahavidyalaya, Gunjoti Tq. Omerga Osmanabad Maharashtra 413606 for providing LCR-Qmeter facility for the characterization of dielectric data for the present investigation.

References

[1] P. Saravanan, K. Jayamoorthy, S. Anandakumar, Fluorescence quenching of APTES by Fe2O3 nanoparticles–Sensor and antibacterial applications, Journal of Luminescence, 178 (2016) 241-248.
[2] K. K Rama, K. K Vijaya, R. Dachepalli, Structural and electrical conductivity studies in nickel-zinc ferrite, Advances in Materials physics and chemistry, 2012 (2012).
[3] S. Mansour, M. Abdo, F. Kzar, Effect of Cr dopant on the structural, magnetic and dielectric properties of Cu-Zn nanoferrites, Journal of Magnetism and Magnetic Materials, 465 (2018) 176-185.
[4] N. Gupta, A. Verma, S.C. Kashyap, D. Dube, Microstructural, dielectric and magnetic behavior of spin-deposited nanocrystalline nickel–zinc ferrite thin films for microwave applications, Journal of Magnetism and Magnetic Materials, 308 (2007) 137-142.
[5] P.B. Kharat, A.V. Humbe, J.S. Kounsalye, K.J.J.o.S. Jadhav, N. Magnetism, Thermophysical investigations of ultrasonically assisted magnetic nanofluids for heat transfer, 32 (2019) 1307-1317.
[6] N.P. Cook, P. Schwaninger, H. Widmer, Ferrite antennas for Google wireless power transfer, Google Patents, 2013.
[7] M. Shisode, P.B. Kharat, D.N. Bhoyar, V. Vinayak, M. Babrekar, K. Jadhav, Structural and multiferroic properties of Ba2+ doped BiFeO3 nanoparticles synthesized via sol-gel method, AIP Conference Proceedings, AIP Publishing LLC, 2018, pp. 030276.
[8] B.V. Prasad, K. Ramesh, A. Srinivas, Structural and magnetic studies of nano-crystalline ferrites MFe 2 O 4 (M= Zn, Ni, Cu, and Co) synthesized via citrate gel auto combustion method, Journal of superconductivity and Novel magnetism, 30 (2017) 3523-3535.
[9] M.V. Khedkar, S.A. Jadhav, S.B. Somvanshi, P.B. Kharat, K.J.S.A.S. Jadhav, Physicochemical properties of ambient pressure dried surface modified silica aerogels: effect of pH variation, 2 (2020) 1-10.
[10] A. Lipare, P. Vasambekar, A. Vaingankar, Effect of LiCl doping on dielectric behavior of copper–zinc ferrite system, Journal of magnetism and magnetic materials, 279 (2004) 160-172.
[11] S. Qamar, M.N. Akhtar, K.M. Batoe, E.H. Raslan, Structural and magnetic features of Ce doped Co-Cu-Zn spinel nanoferrites prepared using sol gel self-ignition method, Ceramics International, DOI (2020).
[12] M.V. Shisode, A.V. Humbe, P.B. Kharat, K.J.J.o.E.M. Jadhav, Influence of Ba $^{2+}$ on opto-electric properties of nanocrystalline BiFeO$_3$ multiferroic, 48 (2019) 358-367.

[13] N.K. Gupta, Y. Ghaifari, S. Kim, J. Bae, K.S. Kim, M. Saiufuddin, Photocatalytic Degradation of Organic Pollutants over MFe$_2$O$_4$ (M= Co, Ni, Cu, Zn) Nanoparticles at Neutral pH, Scientific reports, 10 (2020) 1-11.

[14] S.B. Somvanshi, S.R. Patade, D.D. Andhare, S.A. Jadhav, M.V. Khedkar, P.B. Kharat, P.P. Kirade, K.J.J.o.A. Jadhav, Compounds, Hyperthermic evaluation of oleic acid coated nano-spinel magnesium ferrite: enhancement via hydrophobic-to-hydrophilic surface transformation, DOI (2020) 155422.

[15] M.A. Yousuf, S. Jabeen, M.N. Shahi, M.A. Khan, I. Shakir, M.F. Warsi, Magnetic and electrical properties of yttrium substituted manganese ferrite nanoparticles prepared via micro-emulsion route, Results in Physics, 16 (2020) 102973.

[16] P. Palade, C. Comanescu, A. Kuncser, D. Berger, C. Matei, N. Iacob, V. Kuncser, Mesoporous Cobalt Ferrite Nanosystems Obtained by Surfactant-Assisted Hydrothermal Method: Tuning Morpho-structural and Magnetic Properties via pH-Variation, Nanomaterials, 10 (2020) 476.

[17] A. Singh, P. Chauhan, Structural, electrical and optical properties of Mn0.2Co0.8Fe2O4 nano ferrites, Materials Today: Proceedings, DOI (2020), 2020-2018.

[18] S.R. Patade, D.D. Andhare, P.B. Kharat, A.V. Humbe, K.J.C.P.L. Jadhav, Impact of crystallites on enhancement of bandgap of Mn$_{1-x}$ZnxFe2O4 ($0 \leq x \leq 0$) nanospinels, 745 (2020) 137240.

[19] H. Shashidharagowda, S.N. Mathad, Effect of incorporation of copper on structural properties of spinel nickel manganites by co-precipitation method, Materials Science for Energy Technologies, 3 (2020) 201-208.

[20] P.B. Kharat, A.R. Chavan, A.V. Humbe, K.J.J.o.M.S.M.i.E. Jadhav, Evaluation of thermoacoustics parameters of CoFe$_2$O$_4$–ethylene glycol nanofluid using ultrasonic velocity technique, 30 (2019) 1175-1186.

[21] M. Almessiere, Y. Slimani, H. Güngüneş, V. Kostishyn, S. Trukhanov, A. Trukhanov, A. Baykal, Impact of Eu$^{3+}$ ion substitution on structural, magnetic and microwave traits of Ni–Cu–Zn spinel ferrites, Ceramics International, DOI (2020).

[22] D. Allam, S. Bennici, L. Limousy, S. Hocine, Improved Cu-and Zn-based catalysts for CO2 hydrogenation to methanol, Comptes Rendus Chimie, 22 (2019) 227-237.

[23] J. Liu, Y. Liu, W. Yan, D. Yang, J. Fan, W. Huang, Effect of zinc source on the ethanol synthesis from syngas over a slurry CuZnAl catalyst, International Journal of Hydrogen Energy, DOI (2020).

[24] W. Zhang, A. Sun, X. Zhao, X. Pan, Y. Han, N. Suo, L. Yu, Z. Zuo, Structural and magnetic properties of Ni–Cu–Co ferrites prepared from sol-gel auto combustion method with different complexing agents, Journal of Alloys and Compounds, 816 (2020) 152501.

[25] S. Kanagesan, M. Hashim, S. AB Aziz, I. Ismail, S. Tamilselvan, N.B. Alitheen, M.K. Swamy, B. Purna Chandra Rao, Evaluation of antioxidant and cytotoxicity activities of copper ferrite (CuFe2O4) and zinc ferrite (ZnFe2O4) nanoparticles synthesized by sol-gel self-combustion method, Applied Sciences, 6 (2016) 184.

[26] A. Abdeen, Electric conduction in Ni–Zn ferrites, Journal of magnetism and magnetic materials, 185 (1998) 199-206.

[27] A.R. Lamani, H. Jayanna, P. Parameswara, R. Somashekar, Microcrystalline parameters of Cu-Zn ferrites using X-ray line profile analysis, DOI (2009).

[28] R. Kulkarni, V. Patil, Magnetic ordering in Cu-Zn ferrite, Journal of Materials Science, 17 (1982) 843-848.

[29] A. Gholizadeh, E. Jafari, Effects of sintering atmosphere and temperature on structural and magnetic properties of Ni-Cu-Zn ferrite nano-particles: Magnetic enhancement by a reducing atmosphere, Journal of Magnetism and Magnetic Materials, 422 (2017) 328-336.

[30] A. Sattar, S.A. Rahman, Dielectric properties of rare earth substituted Cu–Zn ferrites, physica status solidi (a), 200 (2003) 415-422.