

A review on influence of certain additives on properties of Ni-Cu-Zn ferrites.

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ABSTRACT

Ni-Cu-Zn ferrites are a versatile class of soft ferrite materials with spinel crystal structure. By controlling the method of preparation, types of additives, composition, sintering condition and substitution levels it is possible to tailor the properties of Ni-Cu-Zn ferrites to specific application. To investigate the structural properties XRD, FTIR and SEM techniques are used. The magnetization is measured using VSM technique. The substitution of Additives such as Co, Mn, Mg, Al and rare earth ions increases the magnetic properties. Additives also influences the distribution of cations between A and B sites, which may leads a slight change in lattice parameters and unit cell volume.

1 Introduction

Magnetic ceramics with iron oxide as the major constituent are termed as ferrites. Ferrites are a class of magnetic materials that exhibit a unique combination of properties, making them highly valuable for various technological applications. Today ferrites have truly wide range of potential applications, and have contributed materially to the advances in electronics. In the area of new materials, ferrites with permeability up to 30,000 and power ferrites for frequencies up to 10 MHz have been made available commercially [1]. It is a well-known fact that the properties of ferrites are sensitive to method of preparation, substitution of cations, microstructure, sintering time, temperature and mostly on distribution of cations on the tetrahedral (A) and octahedral sites (B) in the spinel lattice with the general formula AB_2O_4 [2].

NiCuZn ferrite has the spinel structure. Spinel has the general formula MFe_2O_4 , where M is divalent metal ion. The spinel lattice consists of an oxygen closed-packed arrangement in which 32 oxygen ions form a unit cell. Two kinds of interstices in between the closed-packed anions. a) Tetrahedrally coordinated interstices (called 'A' site) and b) octahedrally coordinated interstices (called 'B' site). Structurally spinel can be represented as AB_2O_4 . One unit cell of it contains eight formula units of AB_2O_4 , where, out of 64 'A' sites 8 and out of 32 'B' sites 16 are occupied by cations. The electromagnetic properties of NiCuZn ferrites are

highly sensitive to the processing parameters especially sintering conditions and the amount of constituent metal oxides in their composition. There are several methods available to synthesize appropriate ferrites with tailor-made properties. Physical and chemical methods used in ferrite synthesis are – mechanical alloying, high energy milling, inert gas condensation, citrate/glycine precursor method, molten salt method, plasma deposition method, hydrothermal reaction, chemical co-precipitation, and sol-gel technique [3-5].

The properties of ferrites are a complex interplay of various factors, including their chemical composition, synthesis method, and microstructural features. Key influencing parameters include the specific elements and their ratios within the ferrite structure, the techniques used to prepare the ferrite material, the introduction or replacement of ions within the ferrite lattice, and the conditions employed during the sintering process. Furthermore, the electronic configuration of the metal ions occupying the tetrahedral (A) and octahedral (B) sites within the ferrite structure significantly influences their physical properties. These ions, with their varying oxidation states, contribute to the unique magnetic and electrical behavior of ferrites. To enhance the desired properties of ferrites, various approaches have been explored. One common strategy involves the incorporation of suitable non-magnetic or diamagnetic impurities into the A or B sites of the ferrite lattice. This method has demonstrated the potential to improve the electrical, magnetic, and optical properties of ferrites [6,7]. Considering the scope many

researchers investigate for various compositions in the system (NiCuZn)Fe₂O₄. The work on different ions substituted in NiCuZn ferrite is observed multidisciplinary in nature. In the present article Some investigations in last few years has been reviewed keeping a view that some useful result may come up in the contest of research and development.

2 Experimental Findings

Spinel ferrites can be fabricated using a variety of methods, including solid-state reaction [10], high-energy ball milling [8], sol-gel processes [9], chemical co-precipitation, microwave sintering, auto-combustion, conventional ceramic techniques, and two-step synthesis approaches. Among these, the solid-state reaction method has been extensively utilized by researchers for the synthesis of Ni-Cu-Zn ferrites [10-12]. Numerous research efforts have centred on enhancing the electromagnetic properties of ferrites through the substitution of different ions.

2.1 Influence of substituting Co

Byun et al. [13] investigated the electromagnetic properties of (Ni_{0.2}Cu_{0.2}Zn_{0.6})_{1.02-x}Co_xFe_{1.98}O₄ ferrites. The substitution of Co ions into the Ni-Cu-Zn ferrite system significantly impacts its magnetic and electrical properties. Studies have shown that Co substitution can:

Increase saturation magnetization: Co has a higher magnetic moment than Zn, leading to an increase in the overall magnetization of the ferrite.[14]

Enhance magnetic anisotropy: The presence of Co ions introduces uniaxial anisotropy, which can improve the magnetic properties of the ferrite, such as coercivity and remanence [15].

Influence electrical resistivity: Co substitution can affect the electrical resistivity of the ferrite, which is crucial for high-frequency applications [16].

2.2 Influence of substituting Mg

Extensive research has investigated the influence of Mg substitution on the properties of various ferrite systems. These studies have consistently demonstrated that Mg substitution can significantly alter the structural, electrical, and magnetic characteristics of these materials. MgO, a highly stable oxide, finds applications in a wide range of technological domains[17]. Mg substitution in Ni-Cu-Zn ferrites has been shown to significantly influence their magnetic and electrical properties. Studies have reported that the incorporation of Mg ions can:

Decrease saturation magnetization: Mg, being diamagnetic, dilutes the magnetic moment of the ferrite, resulting in a decrease in saturation magnetization and The intrinsic coercivity has maximum at x=0.2 due to presence of Fe²⁺ ions and decreases after that [18]. The highest saturation magnetization was found in the composition Ni_{0.3}Cu_{0.2}Zn_{0.3}Mg_{0.2}Fe₂O₄ [19].

Increase resistivity: Mg substitution can enhance the electrical resistivity of Ni-Cu-Zn ferrites, which is beneficial for high-frequency applications.

Alter magnetic anisotropy: The presence of Mg ions can modify the magnetic anisotropy of the ferrite, affecting its magnetic properties.

Influence structural properties: Mg substitution can affect the lattice parameter and microstructure of the ferrite, which can in turn influence its magnetic and electrical properties.

2.3 Influence of substituting Mn

The influence of Mn in NiCuZn ferrite nanoparticles was examined on a series of Ni_{0.5-x}Mn_xCu_{0.2}Zn_{0.3}Fe₂O₄ that was synthesized by sol-gel auto-combustion technique. Site occupancy data revealed that Mn and Zn occupy A-site whereas Ni and Cu occupy B-site. Saturation magnetization increased with increasing Mn content. This is likely due to: Changes in the cation distribution, which can affect the magnetic interactions between the ions. Increased bulk density, leading to a higher number of magnetic moments per unit volume. Due to substitution of Mn on NiCuZn ferrite Dielectric constant and permeability increased that happens leads to reduced grain boundaries and increased density [20].

Li et al. [21] studied the impact of Mn doping on the magnetic and microstructural properties of (Ni_{0.2}Cu_{0.2}Zn_{0.6})_{1.03}(Fe₂O₃)_{0.97}+0.97xMnO₂ ferrites. Their research revealed that increasing Mn content initially led to an enhancement in initial permeability. However, when Mn content exceeded 0.4, the formation of a secondary phase was observed. This higher Mn concentration resulted in an increase in grain size within the Ni-Cu-Zn ferrite. Consequently, the fraction of grain boundaries, which typically exhibit high resistance, decreased. This reduction in grain boundary resistance ultimately lowered the overall resistivity of the material.

2.4 Influence of substituting Rare earth ions

Rare earth-substituted ferrites have shown great promise for a wide range of applications. Introducing small quantities of rare earth ions into ferrite materials can significantly alter their magnetic, electrical, and structural characteristics. The specific changes observed are highly dependent on the type and concentration of the rare earth element employed. Numerous studies have explored the effects of various rare earth atoms (including Dy, Ce, Th, La, Sm, Gd, Nd, Tb, Y, and Eu) on the properties of ferrites. These investigations have consistently demonstrated that different rare earth elements exhibit distinct behaviors when incorporated into the spinel ferrite structure.

The study investigated the effect of rare earth (Nd and La) doping on the structural, magnetic, and dielectric properties of Ni-Cu-Zn ferrite nanoparticles synthesized using the sol-gel auto-ignition method [22]. Rare earth doping increased unit cell size, specific surface area, and decreased porosity. Cation distribution analysis revealed Ni²⁺ at A-sites, and Ni²⁺, La³⁺, Nd³⁺ at B-sites, while Fe³⁺ occupied both A and B sites. Saturation magnetization (Ms) decreased significantly from 85 to 31 emu/g due to weakened A-B interactions. Coercivity (Hc) increased from 27 to 98 Oe.

Dielectric constant (ϵ') increased substantially from 570 to 1090 at low frequencies (up to 10 kHz). Dielectric loss slightly decreased with rare earth doping.

Ni-Cu-Zn ferrite nanoparticles doped with varying amounts of Dy³⁺ were synthesized using an ultra-sonication assisted sol-gel method. XRD confirmed the cubic spinel structure, while FT-IR revealed characteristic vibrational bands. Magnetic studies showed soft ferromagnetic behaviour with initial increases in saturation magnetization (M_s) and remnant magnetization (M_r) followed by a decrease with increasing Dy³⁺ content. FC/ZFC measurements indicated spin glass behaviour with an irreversible temperature above 300 K. Mossbauer spectroscopy confirmed the occupation of octahedral sites by Dy³⁺ ions. Optical analysis revealed a direct band gap between 1.69 and 2.33 eV, with all samples exhibiting light absorption in the visible region as confirmed by diffuse reflectance spectroscopy [23].

Junaid et.al [24] have studied the Structural, spectral, dielectric and magnetic properties of indium substituted copper spinel ferrites synthesized via sol gel technique and characterize them using TGA/DTA, XRD. They observed that the value of M_s and H_c are reduced with the substitution of In³⁺ ions.

Akhtar M. N. et al [25] studied the effect of rare earth doping on the structural and magnetic features of nano-crystalline spinel ferrites prepared via sol gel route and observed that the crystallite size, lattice constant and volume of cell decreased. X-ray density, bulk density and porosity are also decreases. The doping increased Ni-Zn ferrites versatility in industrial and technological applications.

Dasan et. al [26] studied influence of La³⁺ substitution on properties of Ni-Zn ferrites and observed that the saturation magnetization (M_s) and coercivity (H_c) of La³⁺ substituted samples decreased as compared to the Ni-Zn ferrite samples. It means La ion substitution influenced structural magnetic and dielectric property.

B. B. V. S. Vara Prasad et. al [27] studied effect of indium substitution on magnetic properties on Ni-Zn ferrites. The saturation magnetization and Curie temperature decreases with indium content. Dielectric constant and loss factor increased initially and then decreased

Jacobo and Bercoff [28] studied the structure and electromagnetic properties of Y³⁺-substituted Ni-Zn spinels prepared by a sol-gel method. Y³⁺ substitution slightly reduces the average crystallite size and unit cell parameters, and it modifies the saturation magnetization, permeability, and permittivity. The dielectric constant decreases with the Y content, showing a constant behavior in the explored frequency range.

Liu et al. [29] explored the doping effect of Sm³⁺ on the magnetic and dielectric properties of Ni-Zn spinels. Ni_{0.5}Zn_{0.5}Sm_xFe_{2-x}O₄ samples were synthesized by a conventional two-step solid sintering method. It was found that the substitution by the Sm³⁺ cations decreased the dielectric loss in the frequency range of 1–100 MHz, increased in the frequency range of 100–1000 MHz.

Munirah Abdullah Almessiere et al [30] studied the Influence of Dy³⁺ ions on the Microstructures and Magnetic, Electrical, and Microwave Properties of [Ni_{0.4}Cu_{0.2}Zn_{0.4}](Fe_{2-x}Dy_x)O₄ (0.00 ≤ x ≤ 0.04) Spinel Ferrites and investigated their electrical and magnetic properties,

M Raghassudha et al [31] studied Structural and dielectric properties of Indium substituted Ni-Cu-Zn ferrites Ni_{0.5}Cu_{0.25}Zn_{0.25}Fe_{2-x}In_xO₄ and characterized using XRD, SEM. Dielectric properties are investigated in detail.

Mohd. Hashim et. al [32] investigated high temperature dielectric studies of indium-substituted NiCuZn nanoferrites. The dielectric constant and dielectric loss tangent exhibited decreasing trends as the frequency increased at selected temperatures for all of the compositions.

A M Shahare et al [33] have studied Structural, electric and magnetic properties of Ce-substituted Ni-Cu-Zn ferrite and characterized them using XRD, SEM, and VSM. They observed a decrease in Saturation magnetization (M_s), Remanent magnetization (M_r) and increase in Coercivity (H_c) with Ce content. AC Conductivity is found to increase with the Ce content.

3 Conclusion

This review highlights the significant influence of various ion substitutions (Co, Mg, Mn, and rare earths) on the structural, magnetic and electrical properties of Ni-Cu-Zn ferrites. Co substitution generally enhances saturation magnetization and magnetic anisotropy. Mg substitution typically leads to a decrease in saturation magnetization and an increase in resistivity. Mn substitution can increase saturation magnetization, dielectric constant, and permeability, while also influencing grain growth. Rare earth substitutions such as La, Nd, and Dy significantly impact magnetic properties, altering saturation magnetization, coercivity and inducing magnetic anisotropy. Furthermore, rare earth doping can influence structural parameters, dielectric properties, and optical behaviour. These findings demonstrate that ion substitution provides a powerful tool for tailoring the properties of Ni-Cu-Zn ferrites for specific applications such as high-frequency devices, magnetic recording media, and sensors.

References:

- [1] Goldman A., "Recent Advances in Ferrite Materials Technology," in Modern Ferrite Technology, Van Nostrand Reinhold, New York, (1990).
- [2] M. Penchal Reddy, W. Madhuri, N. Ramamanohar Reddy, K.V. Siva Kumar, V.R.K. Murthy, R. Ramakrishna Reddy, Materials Science and Engineering C 30 (2010) 1094.
- [3] M.C. Dimri, A. Verma, S.C. Kashyap, D.C. Dube, O.P. Thakur, C. Prakash, Mater. Sci. Eng., B 133 (2006) 42–48.

- [4] S.M. Kabbur, U.R. Ghodake, R.C. Kambale, S.D. Sartale, L.P. Chikhale, S.S. Suryavanshi, J. Electron. Mater. 46 (2017) 5693–5704.
- [5] S.E. Shirsath, D. Wang, S.S. Jadhav, M.L. Mane, S. Li, Ferrites obtained by sol-gel method, in: L. Klein, M. Aparicio, A. Jitianu (Eds.), Handbook of Sol-Gel Science and Technology, Springer, Cham, 2018, pp. 695–735.
- [6] A. Goldman, Handbook of Modern Ferromagnetic Materials, (Springer Science + Business Media, New York, 1999).
- [7] J. Smith, and Wegn, Ferrites, (John Wiley and Sons Pub., The Netherlands, 1959).
- [8] S. K. Sharma, R. Kumar, S. Kumar, M. Knobel, C. T. Meneses, V. V. Siva Kumar, V. R. Reddy, M. Singh, and C. G. Lee, J. Phys.: Condens. Matter. 20, 235214 (2008).
- [9] S. Zahi, M. Hashim, and A. R. Daud, J. Magn. Magn. Mater. 308, 177 (2007).
- [10] O. F. Caltun, L. Spinu, Al. Stancu, L. D. Thung, and W. Zhou, J. Magn. Magn. Mater. 160, 242 (2002). [11] A. Barba, C. Clausell, C. Feliu, and M. Monzo, J. Am. Ceram. Soc. 87 (4), 571 (2004).
- [12] H. M. Sung, C. J. Chen, W. S. Ko, and H. C. Lin, IEEE Trans. Magn. 30 (6), 4906 (1994).
- [13] T. Y. Byun, S. C. Byeon, and K. S. Hong, IEEE Trans. Magn. 35 (5), 3445 (1999).
- [14] J. Kulikowski and A. Bienkowski, J. Magn. Magn. Mater. 41, 63 (1984).
- [15] J. Xiang, X. Shen, and X. Meng, Mat. Chem. Phys. 114 (1), 362 (2009).
- [16] S.M. Kabbura, D.Y. Nadargib, R.C. Kambalec, U.R. Ghodakea, JMMM, **Volume 517**, , 167376 1 January 2021
- [17] A. M. E. Raj, T. Som, V. Ganesan, M. Jayachandran, G. Selvan, V. Swaminathan, and C. Sanjeeviraja, Nucl. Instr. Meth. Phys. Res. B 266, 2564 (2008).
- [18] Ch. Sujatha a,n, K. Venugopal Reddy a, K. Sowri Babu a, A. RamaChandra Reddy a, M. Buchi Suresh b, K.H. Rao, JMMM 340, 38-45 (2013)
- [19] M.A. Gabal, JMMM 321,3144-3148 (2009)
- [20] Gaikwad, A.A., Kulkarni, S.B. Enhanced Magnetic and Permeability Properties of Mn-Substituted NiCuZn Nanoparticles for Ferrite Core Application. *J Supercond Nov Magn* **34**, 2405–2414 (2021).
- [21] B. Li, Z. X. Yue, X. W. Qi, J. Zhou, Z. L. Gui, and L. T. Li, Mat. Sci. Engg. B **99**, 252 (2003).
- [22] B.B. Raje Shaikh, Bhagwan G. Toksha, Sagar E. Shirsath, Aniruddha Chatterjee, Shyam Tonde, Syed Qadeeruddin Chishty, JMMM, Volume 537, 2021,
- [23] Ayse Demir Korkmaz, Physica B: Condensed Matter, Volume 654, 414741, 2023,
- [24] Junaid, M., Khan, M.A., Abubshait, S.A., Akhtar, M.N., Kattan, N.A., Laref, A. and Javed, H.M.A.: *Ceramics International*, 46(17), pp.27410-27418, (2020)
- [25] Akhtar, M.N. and Khan, M.A.: *Journal of Magnetism and Magnetic Materials*, 460, pp.268-277, (2018)
- [26] Dasan, Y.K., Guan, B.H., Zahari, M.H. and Chuan, L.K.: *PloS one*, 12(1), p.e0170075. (2017)
- [27] B. B. V. S. Vara Prasad.: *J Theor Appl Phys* 9:267–272, (2015)
- [28] Jacobo, S. E.; Bercoff, P. G. *Ceram. Int.*, 42, 7664–7668, 2016.
- [29] Liu, Z.; Peng, Z.; Lv, C.; Fu, X. *Ceram. Int.* 43, 1449–1454, 2017.
- [30] Munirah Abdullah Almessiere, Yassine Slimani, Hakan Güngüneş, Ayse Demir Korkmaz, Tatiana Zubar, Sergei Trukhanov, Alex Trukhanov, Ayyar Manikandan, Fatimah Alahmari, and Abdulhadi Baykal: *ACS Omega* 6, 10266–10280, (2021).
- [31] M Raghassudha, P Veerasomaiah: *International Journal of Conceptions on Computing and Information Technology* Vol. 3, Issue. 1, 48, April' 2015.
- [32] Mohd. Hashim, M. Raghassudha, Jyoti Shah, Sagar E. Shirsath, D. Ravinder, Shalendra Kumar, Sher Singh Meena, Pramod Bhatt, Alimuddin, Ravi Kumar, R.K. Kotnala: *Journal of Physics and Chemistry of Solids* 112, 29–36, (2018).
- [33] A M Shahare, D S Choudhary, A V Bagde, A S Nagpure: *Science, Technology and Development*, Volume VIII, Issue X, 464, (2019).