

Effect of V₂O₅ Additive on Electrical and Dielectrical Properties of Ni-Zn ferrite

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Abstract: In this work, the electrical and dielectrical properties of Ni-Zn ferrite by addition of additive V₂O₅ powders were investigated. Ni_{0.7}Zn_{0.3}Fe₂O₄+ xV₂O₅ (where x = 0.0 and 0.2) powders were prepared by solid state reaction method. The DC electrical resistivity decreases with increase in temperature obeying Arrhenius relation. The variation of DC resistivity with temperature shows change in conduction behavior at Curie temperature. The activation energy in paramagnetic region is more than that of ferrimagnetic region. The room temperature resistivity of V⁵⁺ substituted Ni-Zn ferrites is higher than pure spinel ferrite. The resistivity decreases with V₂O₅ addition. The dielectric constant and dielectric loss tangent decreased with the increase of V⁵⁺ content. The obtained electrical and dielectric parameters are useful for high frequency application.

Keywords: Ni-Zn ferrite, V₂O₅ additive, electrical and dielectrical.

I. INTRODUCTION

Ferrites are important class of ferromagnetic material which is considered as highly important electric materials used widely in electronic industries, information, and communication technology. According to the demands of modern society the ferrites are capable to play important role in the modern society. So a constant challenge is being posted by ever increasing demands for ferrite materials in home communication appliance, computer, electrical and other technical field [1]. The interest in this oxide emerges from their versatile applicability in the relative to microwave frequency region. Spinel ferrites are a large group of materials with uniquely wide range of various properties such as electronic, electrical [2]. On the basis of their excellent electrical and magnetic properties they are used in application such as inductor, transformer core, antenna rod, magnetic recording etc. Regarding to the applications, the most important properties of spinel ferrites are conductivity and type of dominant charge carriers, saturation magnetization, coercivity etc. The spinel exhibits relatively high resistivity at carrier frequency, sufficiently low eddy current and dielectric loss for microwave applications. These material are extensively used in microwave devices, computer memory chip magnetic recording media etc [3]. Mostly these electrical and magnetic properties depend on method of preparation, preparative parameters, preparative conditions, particle size, nature of dopant etc [4].

Crystallographic and magnetic properties of V₂O₅ doped titanium cobalt ferrites were investigated by many researcher and found that the average grain size of the samples increases with V₂O₅ concentration [5]. Microstructure and magnetic properties of Ni-Zn ferrites doped with MnO₂ have been reported in the literature. The study reveals that the average grain size, sintering density and real permeability gradually decrease with the increase of the MnO₂ content [6]. Substituted Ni-Zn ferrites for passive sensors application were synthesized and it is reported that the influence of small Cu substitution on various magnetic properties of Ni-Zn ferrites has been analyzed by means of various experimental methods and interpreted from the point of view of preparation technology optimization and possible applications of such materials in sensor technology. A strong correlation between the substituent content and resulting properties has been observed [7]. The effect of additive on the microstructure and complex permeability of Ni-Zn ferrites were investigated and observed that vanadium additions results in fine grain structures whereas niobium additions promoted grain growth with an increase in grain size [8]. It is reported that the addition of V₂O₅ in the Ni-Zn-Cu ferrite system decreases semiconducting behavior in material and it also report at higher concentration of vanadium and nickel decrease in the conductivity due to addition of V⁵⁺ ion into the lattice may be segregate near the grain boundaries thereby increase its effective thickness and decreasing in conductivity [9]. It is also reported that Increase in the concentration of the V₂O₅ in Ni-Zn spinel ferrite results in increase in the resistivity due to the addition of V₂O₅, V⁵⁺ ions occupy B-sites in ferrite so there is hopping in ferric ion from Fe²⁺ to Fe⁺³ [8]. Thus, it is revealed from the literature that the additives like V₂O₅, influences the structural and electrical properties of spinel ferrites. In our previous study, we have reported the effect of V₂O₅ additive on structural and magnetic properties of Ni-Zn ferrite [10].

Therefore, attempt has been made to investigate the electrical and dielectrical properties of V_2O_5 added $Ni_{0.7}Zn_{0.3}Fe_2O_4$ spinel ferrite system and the results are presented in this work.

II. EXPERIMENTAL

Polycrystalline ferrite with the formula $(Ni_{0.7}Zn_{0.3}Fe_2O_4+xV_2O_5)$ with ($x = 0.0$ and 0.2) have been prepared by conventional ceramic technique. Nickel oxide, Ferric oxide, Zinc oxide and Vanadium oxide were taken in stoichiometric ratio to synthesize $Ni_{0.7}Zn_{0.3}Fe_2O_4+xV_2O_5$. The precursors were mixed thoroughly using mortar and pestle, in an air atmosphere for 1.5 h so as to make a homogeneous fine powder. Solid-state reaction was carried out in an air atmosphere. The pre-sintering of the samples were carried out at $950\text{ }^\circ\text{C}$ for 6 h and. The presintered oxides were ground finely. Then the samples were finally sintered $1080\text{ }^\circ\text{C}$ to improve the homogeneity. finally, the samples were press into pallets using hydraulic press at a constant pressure of 5 tons and sintered at $1100\text{ }^\circ\text{C}$ for 10 h and the slowly cooled at room temperature.

The electrical measurements were carried out in the temperature range $300\text{ K} - 800\text{ K}$ using two probe techniques. The dielectric measurements were carried out at room temperature and as a function of frequency using LCR- Q meter. The measurements were carried out on the samples in the form of disc with polished surfaces covered by silver paste. The dimensions of the disc shaped pellets are 10 mm in diameter and 3 mm thickness.

III. RESULTS AND DISCUSSIONS

The XRD patterns confirm the formation of cubic spinel type lattice of the prepared samples as reported in our previous work.

Microstructure and chemical composition play a pivotal role in altering the dielectric loss, resistivity, and dielectric constant of the material [11]. Hopping mechanism is the major contributor for conduction in ferrites. According to the band theory, the change in the concentration of charge carrier with temperature is the main reason of conduction. But in ferrites, the conduction increases with temperature due to the increase in hopping of ion between the B-B sites [12].

In the present work, DC resistivity was measured using the two-probe method against different temperatures. Fig. 1 shows the DC resistivity plots as a function of reciprocal of temperature for the prepared samples. The decrease in the resistivity with increase in temperature is in accordance with the ion hopping mechanism. The mobility of charge carriers is increasing with both, i.e. temperature and composition [13].

Figure 1 shows plot of logarithm of resistivity against reciprocal of temperature. The graph shows two activation regions similar to those which have been reported in other spinel ferrites structures [14].

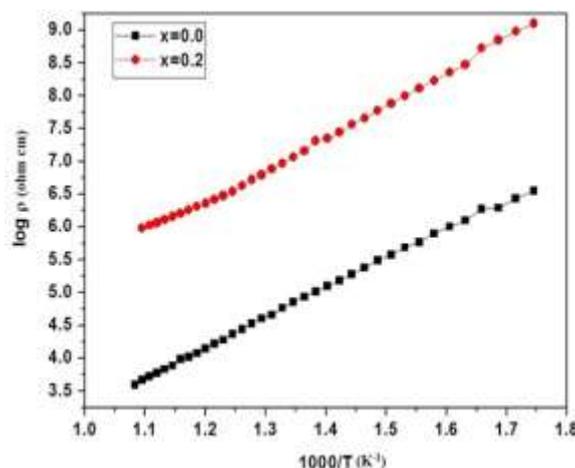


Fig.1. Variation of DC Resistivity with reciprocal of temperature for $Ni_{0.7}Zn_{0.3}Fe_2O_4+xV_2O_5$ ($x = 0.0$ and 0.2) samples

The first region (paramagnetic, corresponding to higher temperature) is due to impurities and voids. The second region (ferrimagnetic, corresponding to lower temperature) is the ferromagnetic conduction region. The activation energies of the ferrites were calculated with the help of Arrhenius relation as given in eq. (1) [15].

$$\sigma = \sigma_0 \exp\left(-\frac{E_g}{kT}\right) \quad (1)$$

where ρ is the resistivity at a given temperature T , k_B is the Boltzmann constant, and E_g is the activation energy. The activation energies determined for the present samples are 1.3348 and 0.2408 eV which are given in table 1. It is observed from figure 1 that resistivity decreases with increase in temperature. The variation of $\log \rho$ against the

reciprocal of the temperature in the low temperature range is markedly different from that in the relatively high temperature range. Verwey and de Boer [16] establish that electronic exchange ($Fe^{2+} \leftrightarrow Fe^{3+}$) takes place in the crystallographically equivalent site without causing a change in the energy state of the crystal as a result of transition. Hopping between A-A site does not exist because Fe^{2+} ions form during processing preferably occupy octahedral [B] site only. Therefore, Hopping between B-B sites is possible and variation in resistivity can be explained on the basis of hopping mechanism. Similar explanation was also reported in the literature for other spinel ferrite doped with additives [8, 16].

The compositional variation of the resistivity suggests that resistivity increases with increasing concentration of V_2O_5 . With the addition of V_2O_5 the V^{5+} ions occupy octahedral [B] site which limits the degree of Fe^{2+} to Fe^{3+} electron hopping condition results in increase of resistivity. The increase in resistivity may be due to segregation of vanadium at grain boundaries at higher concentration.

Fig. 2 displays the variation of dielectric constant (ϵ') as a function of frequency at room temperature. It is observed from fig. 2 that the dielectric constant decreases exponentially with increase in frequency.

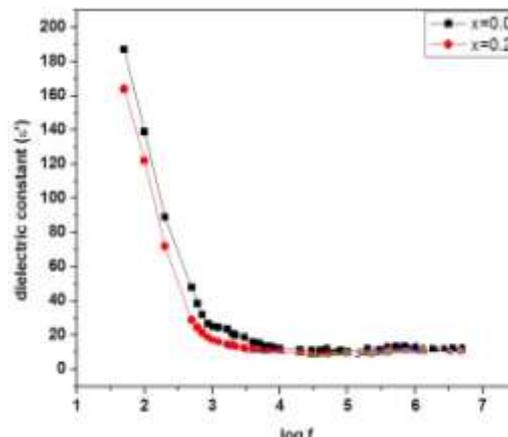


Fig. 2. Variation of Dielectric constant (ϵ') as a function of frequency for $Ni_{0.7}Zn_{0.3}Fe_2O_4+xV_2O_5$ ($x = 0.0$ and 0.2) samples

At low frequency the dielectric constant is greater than the dielectric constant at higher frequency. Samples having high DC electrical resistivity acquire low value of dielectric constant and vice-versa [17]. Generally, dielectric constant decreases with increasing frequency. The decrease of dielectric constant with V^{5+} ion substitution can be explained on the basis of the mechanism of polarization process in ferrites, which is similar to that in the conduction process. A strong correlation between conduction mechanism and dielectric behavior of ferrites has been reported. The whole polarization in ferrites is mainly contributed by the space charge polarization, which is governed by the number of space charge carriers and the conductivity in materials [18] and the hopping exchange of the charges between two localized states and the resultant displacement of the charges with respect to the external field. The addition of V^{5+} ions reduces the iron ions on [B] sites, which is mainly responsible for both space charge polarization and hopping exchange between the localized states. Therefore, increase of V^{5+} content causes a decrease in polarization which is accomplished by a decrease of dielectric constant, ϵ'' , of the composition. Koops has proposed that the effect of grain boundaries is predominant at lower frequencies [19]. The thinner the grain boundary, the higher the dielectric constant is observed. The decrease in dielectric constant with increasing frequency is attributed to the fact that the electron exchange between Fe^{2+} and Fe^{3+} ions cannot follow the change of the external applied field beyond certain frequency [4, 20]. The value of the dielectric constant is very high at lower frequencies and decreases with increasing frequencies. At lower frequencies the grain boundaries are more effective than grain electrical conduction. Similar low values of dielectric constant were found in Mn substituted Ni-Zn ferrites prepared by citrate method [2, 21].

Fig. 3 shows variation of $\tan \delta$ with frequency of present ferrite samples. It is evident from fig 3 that like dielectric constant, dielectric loss tangent also decreases exponentially with increase in frequency. According to Rezlescu the observed relaxation peak may be due to the collective contribution of both p and n type carriers. The conduction mechanism in n type ferrite is considered to be due to hopping of electrons between Fe^{2+} and Fe^{3+} and holes transfer between V^{5+} and V^{4+} in octahedral sites [22]. When the hopping frequency is nearly equal to the frequency of externally applied electric field, a maximum of loss tangent is observed. The decrease of $\tan \delta$ with increasing frequency is attributed to the fact that the hopping frequency of charge carriers cannot follow the changes of the externally applied electric field beyond a certain frequency limit.

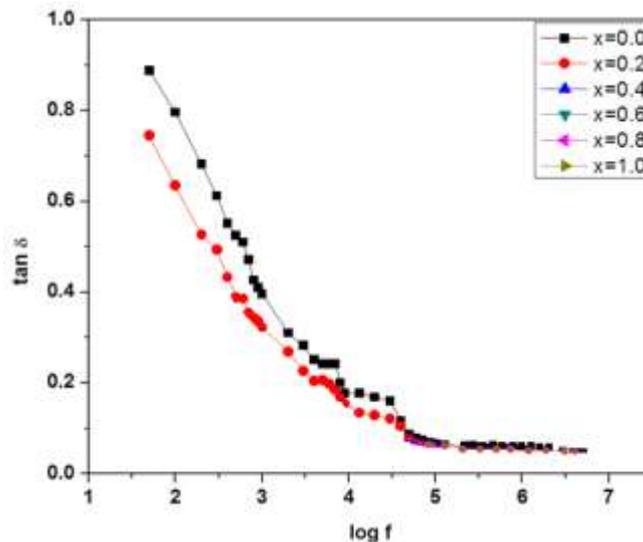


Fig.3.Variation of Dielectric loss tangent ($\tan \delta$) as a function of frequency for $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4+x\text{V}_2\text{O}_5$ ($x = 0.0$ and 0.2) samples

In this case, a maximum in the dielectric loss tangent is observed when the jumping frequency of localized electron approximately becomes equal to that of the externally applied ac electric field. The substitution of V^{5+} ions with addition in place of two Fe^{3+} ions in octahedral B-sites increases the number of electrons hopping between Fe^{2+} and Fe^{3+} (n-type semiconductor ferrite) and holes hopping between Ni^{3+} and Ni^{2+} (p-type semiconductor ferrite), which are responsible for the relaxation processes in the present system.

As the introduction of V^{5+} and present Ni^{2+} ions progresses in the present unit cell, vanadium migrates from octahedral B-sites to tetrahedral A-sites. Therefore, the increase of Ni^{2+} ions at octahedral sites increases the hopping of holes while the replacement of Fe^{3+} with V^{5+} ions leads to the reduction of Fe^{3+} ions content in B-sites, resulting in reducing the electron hopping between Fe^{2+} and Fe^{3+} [23, 24]. It is noticed from Figs.2 and 3 that both dielectric loss and dielectric tangent decrease as the vanadium content increased. This behavior is attributed to the fact that the introduction of vanadium ions entering the lattice may segregate near the grain boundaries. This may lead to increase in the effective thickness, thus decreasing bulk conductivity, which in turn decreases the dielectric loss and dielectric constants [25, 26].

TABLE I Values of Activation energy in ferrimagnetic region (E_f) and paramagnetic region (E_p) for $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4+x\text{V}_2\text{O}_5$ ($x = 0.0 - 1.0$)

| x | (E_f) | (E_p) | $\Delta E = E_p - E_f$ |
|-----|-----------|-----------|------------------------|
| 0.0 | 1.3408 | 1.2149 | 0.1259 |
| 0.2 | 0.2408 | 1.5427 | 1.3019 |

IV. CONCLUSION

The $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4+x\text{V}_2\text{O}_5$ with ($x = 0.0$ and 0.2) spinel ferrites have been synthesized successfully using standard ceramic method. It is observed that the electrical resistivity decreases with increase in temperature obeying Arrhenius relation. The variation of DC resistivity with temperature shows change in conduction behavior at Curie temperature. The activation energy in paramagnetic region is more than that of ferrimagnetic region. The room temperature resistivity of V^{5+} substituted Ni-Zn ferrites is higher than pure spinel ferrite. The resistivity decreases with V_2O_5 addition. The dielectric constant and dielectric loss tangent decreased with the increase of V^{5+} content. The obtained electrical and dielectric parameters are useful for high frequency application.

ACKNOWLEDGEMENT

The authors are very much thankful to Dr. K. M. Jadhav, Professor, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, (M.S.), India for their fruitful guidance and for providing laboratory facilities.

REFERENCES

- [1] M. Sugimoto, The past, present, and future of ferrites, *Journal of the American Ceramic Society*, 82 (1999) 269-280.
- [2] A. Verma, R. Chatterjee, Effect of zinc concentration on the structural, electrical and magnetic properties of mixed Mn–Zn and Ni–Zn ferrites synthesized by the citrate precursor technique, *Journal of magnetism and magnetic materials*, 306 (2006) 313-320.
- [3] A. Goldman, *Modern ferrite technology*, Springer Science & Business Media, 2006.
- [4] I. Gul, W. Ahmed, A. Maqsood, Electrical and magnetic characterization of nanocrystalline Ni–Zn ferrite synthesis by co-precipitation route, *Journal of Magnetism and Magnetic Materials*, 320 (2008) 270-275.
- [5] W.H. Kwon, S.W. Lee, J.-G. Lee, K.P. Chae, Crystallographic and Magnetic Properties of V₂O₅-doped Titanium Cobalt Ferrites, *Journal of the Korean Physical Society*, 55 (2009) 1548-1552.
- [6] S. Hua, H.-W. Zhang, X.-l. Tang, Y.-l. Jing, Microstructure and magnetic properties of Ni-Zn ferrites doped with MnO₂, *Transactions of Nonferrous Metals Society of China*, 21 (2011) 109-113.
- [7] E. Rezlescu, L. Sachelarie, P. Popa, N. Rezlescu, Effect of substitution of divalent ions on the electrical and magnetic properties of Ni-Zn-Me ferrites, *IEEE transactions on magnetics*, 36 (2000) 3962-3967.
- [8] S. Akther, M.A. Choudhury, J. Rahman, Influence of V₂O₅ Addition on the Magnetic and Electrical Properties of Iron-Deficient Ni-Zn Ferrite, *Journal of Bangladesh Academy of Sciences*, 33 (2009) 145-149.
- [9] M. Kaiser, Influence of V₂O₅ ion addition on the conductivity and grain growth of Ni–Zn–Cu ferrites, *Current Applied Physics*, 10 (2010) 975-984.
- [10] M. Patil, M. Sarnaik, V. Murumkar, A. Pandit, D. Shingule, Effect of V₂O₅ Additive on Structural and Magnetic Properties of Ni-Zn ferrite.
- [11] A.I. Kingon, J.-P. Maria, S. Streiffer, Alternative dielectrics to silicon dioxide for memory and logic devices, *Nature*, 406 (2000) 1032-1038.
- [12] E.V. Gopalan, K. Malini, S. Saravanan, D.S. Kumar, Y. Yoshida, M. Anantharaman, Evidence for polaron conduction in nanostructured manganese ferrite, *Journal of Physics D: Applied Physics*, 41 (2008) 185005.
- [13] A. Verma, O. Thakur, C. Prakash, T. Goel, R. Mendiratta, Temperature dependence of electrical properties of nickel–zinc ferrites processed by the citrate precursor technique, *Materials Science and Engineering: B*, 116 (2005) 1-6.
- [14] T. Shinde, A. Gadkari, P. Vasambekar, DC resistivity of Ni–Zn ferrites prepared by oxalate precipitation method, *Materials Chemistry and Physics*, 111 (2008) 87-91.
- [15] P.P. Khirade, S.D. Birajdar, A. Raut, K. Jadhav, Effect of Fe–substitution on phase transformation, optical, electrical and dielectrical properties of BaTiO₃ nanoceramics synthesized by sol-gel auto combustion method, *Journal of Electroceramics*, 37 (2016) 110-120.
- [16] E. Verwey, J. De Boer, Cation arrangement in a few oxides with crystal structures of the spinel type, *Recueil des Travaux Chimiques des Pays-Bas*, 55 (1936) 531-540.
- [17] V. Vinayak, P.P. Khirade, S.D. Birajdar, R. Alange, K. Jadhav, Electrical and dielectrical properties of low-temperature-synthesized nanocrystalline Mg²⁺-substituted cobalt spinel ferrite, *Journal of Superconductivity and Novel Magnetism*, 28 (2015) 3351-3356.
- [18] J. Azadmanjiri, Structural and electromagnetic properties of Ni–Zn ferrites prepared by sol–gel combustion method, *Materials Chemistry and Physics*, 109 (2008) 109-112.
- [19] S. Shenoy, P. Joy, M. Anantharaman, Effect of mechanical milling on the structural, magnetic and dielectric properties of coprecipitated ultrafine zinc ferrite, *Journal of Magnetism and Magnetic Materials*, 269 (2004) 217-226.
- [20] M.C. Dimri, A. Verma, S.C. Kashyap, D. Dube, O. Thakur, C. Prakash, Structural, dielectric and magnetic properties of NiCuZn ferrite grown by citrate precursor method, *Materials Science and Engineering: B*, 133 (2006) 42-48.
- [21] A.K. Singh, T. Goel, R. Mendiratta, O. Thakur, C. Prakash, Dielectric properties of Mn-substituted Ni–Zn ferrites, *Journal of applied physics*, 91 (2002) 6626-6629.
- [22] A. Abdeen, Dielectric behaviour in Ni–Zn ferrites, *Journal of magnetism and magnetic materials*, 192 (1999) 121-129.
- [23] B.P. Rao, K. Rao, G. Sankaranarayana, A. Paduraru, O. Caltuna, Influence of V₂O₅ additions on the resistivity and dielectric properties of nickel-zinc ferrites, *Journal of Optoelectronics and Advanced Materials*, 7 (2005) 697-700.
- [24] G. Jain, B. Das, R. Tripathi, R. Narayan, Influence of V₂O₅ on the densification and the magnetic properties of Ni–Zn ferrite, *Journal of Magnetism and Magnetic Materials*, 14 (1979) 80-86.
- [25] R. Narayan, R. Tripathi, B. Das, G. Jain, Pentavalent vanadium ion addition to Ni-Zn ferrites, *Journal of Materials Science*, 18 (1983) 1934-1940.
- [26] M. Kaiser, Magnetic and dielectric properties of low vanadium doped nickel–zinc–copper ferrites, *Journal of Physics and Chemistry of Solids*, 71 (2010) 1451-1457.