

Electrical Properties of Cu-substituted $\text{Ni}_{0.5-x}\text{Zn}_{0.3}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$ Nanocrystalline Ferrite Prepared by Auto-Combustion Method

Milind Bhandare¹, Gajanan Wagh²

Associate Professor, Department of Physics, Sharadchandra Pawar Mahavidhyalaya, Lonand, MS India¹

Associate Professor, Department of Chemistry, Sharadchandra Pawar Mahavidhyalaya, Lonand, MS India²

ABSTRACT: Ferrites having chemical formula, $\text{Ni}_{0.5-x}\text{Cu}_x\text{Zn}_{0.3}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$ with $x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5 have been prepared by auto-combustion route. Selected area electron diffraction (SAD) patterns confirm the spinel structure of the ferrite. Transmission electron microscopy (TEM) images show a well defined nano-crystallite state with an average particle size of around 34 to 41 nm. The electric properties have been studied by means of DC resistivity. Shows mainly two regions as 303K to 493K (1st region) and above 493K (2nd region). The room temperature resistivity decreases due to the difference in grain size. The conductivity of the specimen increases with increasing copper content. Variation of jump length increases with increase in copper content. The drift mobility increases with increase in Cu-content.

KEYWORDS: Spinel ferrites, DC resistivity, Activation energy, Drift mobility, jump length.

I. INTRODUCTION

Spinel nanocrystalline ferrites are one of the best magnetic semiconductors which have a great importance in telecommunication, microwave and electronics engineering. They are used in variety of applications ranging from simple function devices, like small permanent magnets, to sophisticated device used for the electronic industry [1,2]. Some interesting applications of ferrite materials are found in computer peripherals, telecommunication equipment's, permanent magnets, electronic and microwave devices, magnetic media used in computers, recording devices and magnetic cards. The electrical properties are the most important properties of ferrites, which depend on the processing conditions, sintering temperature, chemical composition and the amount of the additives [3]. High electrical resistivity is characteristics properties of soft ferrites which are not found in traditional soft ferromagnetic materials like silicon, steels or perm alloys [4]. In recent years, nanocrystalline ferrite materials are becoming a subject of intense research because of their unique properties, both from the fundamental and the application point of view [5]. Ferrite with a spinel structure which is formed by a nearly close packed FCC array of anions with holes partly filled by the cations can be represented by the formula MFe_2O_4 where M represents divalent metallic ions located in M interstitial (tetrahedral) sites and Fe metallic ions located in (octahedral) sites. Soft spinel ferrite (MFe_2O_4 , M = Co, Ni, Zn and Mn, etc.) nanoparticles have been intensively investigated due to their remarkable electrical properties and wide practical applications in Ferro-fluids technology magnetic drug delivery, magnetic high-density information storage etc [6, 7].

In the present work materials consists of stoichiometric amounts of AR Grade nickel nitrate [$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], zinc nitrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], magnesium nitrate [$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], copper nitrate [$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$] and iron nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] are mixed together with 10 % aqueous solution of polyvinyl alcohol (PVA) and aqueous solution of sucrose (2 mol per metal ion). This solution is heated slowly at 200 °C for 3h in air atmosphere to form viscous liquid. The evaporation is accompanied by evolution of brown fumes of nitrogen dioxide (NO_2) due to decomposition mixture of nitrates. This distributes the cations throughout the polymer structure so that selective precipitation is prevented during the evaporation process. The energy from the exothermic reaction between oxidant and reductant can be high

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 5, May 2016

enough to form the desired phase within a very short time. In the second step the precursor solution of metal nitrate–PVA–sucrose is evaporated completely to produce black fluffy carbonaceous pyrolysed mass. The carbonaceous dry mass was calcined at 600 °C for 3h. The calcined ferrite powder was granulated using PVA as a binder and were uniaxial pressed for 5 ton/cm² for 5 minutes to produce pellet specimens having 10 mm diameter and 3mm thickness.

The specimens were finally sintered at 800 °C for 4h in air atmosphere.

The aim of our present work is to optimize a composition of the Ni-Cu based ferrite to achieve high resistivity. The high-performance soft magnetic materials prepared using such a simple and low-cost method will be more promising in high-frequency applications and industrialization. Hence in the present paper, we have specially focused on the effect of Cu substitution on micro-structural, and electrical properties were studied and co-related in light of literature in fundamental point of view.

II. EXPERIMENTAL

Ferrite prepared by ceramic method involves high-temperature to complete the solid-state reaction between the constituent oxides or carbonates. The particles obtained by this method are rather large and non-uniform in size. These non-uniform particles, on compacting result in the formation of voids or low density. In order to overcome these difficulties arising due to ceramic method, many researchers have chosen wet chemical method like co-precipitation, hydrothermal processing, auto-combustion etc for production of homogeneous, fine and reproducible ferrites at low temperature. Hence in the present case, we have successfully synthesized Cu substituted Ni-Mg-Zn ferrite using auto-combustion technique. The details about the synthesis parameters and structural analysis are reported in our previous paper [8]. The same samples were further used for the in detail analysis of DC electrical resistivity.

TEM images and selected area electron diffraction (SAD) patterns were carried out by (Model: PHILIPS CM200) with operation voltage 20-200 kV resolution: 2.4 Å. The DC resistivity measurements were carried out using two probe methods. Keithley’s multimeter (model 2000) was used to record current through the sample keeping voltage across the sample constant at room temperature and well above Curie temperature.

The relation between resistivity and temperature is expressed as

$$\rho = \rho_0 \text{Exp}\left(\frac{\Delta E}{k_B T}\right) \dots\dots\dots (1)$$

Where, ρ is the DC electrical resistivity at temperature T,
 K_B is Boltzmann constant

ΔE is activation energy corresponding to electrical process.

Drift mobility μ_d can be calculated using the relation,

$$\mu_d = \frac{1}{ne\rho} \dots\dots\dots (2)$$

where, e = the charge of electron

ρ = the resistivity.

n = the concentration of charge carrier and can be calculated from the equation

$$n = \frac{N \rho_m P_{Fe}}{M} \dots\dots\dots (3)$$

where, M = molecular weight of the sample.

N = the Avogadro’s number.

ρ_m = actual density.

P_{Fe} = the number of iron atoms in the chemical formula of the ferrites.

The jumping length (L) is determined from the relation

$$L = a \frac{\sqrt{2}}{4} \dots\dots\dots (4)$$

where, a is lattice constant obtained from XRD studies.

III.RESULTS AND DISCUSSION

I. TEM STUDY

Transmission electron microscopy (TEM) micrographs are shown in figs.1 (a) and (b) of the nano-sized Ni-Cu ferrite with Cu content of $x=0$ and $x=0.5$. These micrographs are almost spherical in shape and found to be loosely agglomerated. The agglomeration can be attributed to the magnetic dipole interaction arising between ferrite particles

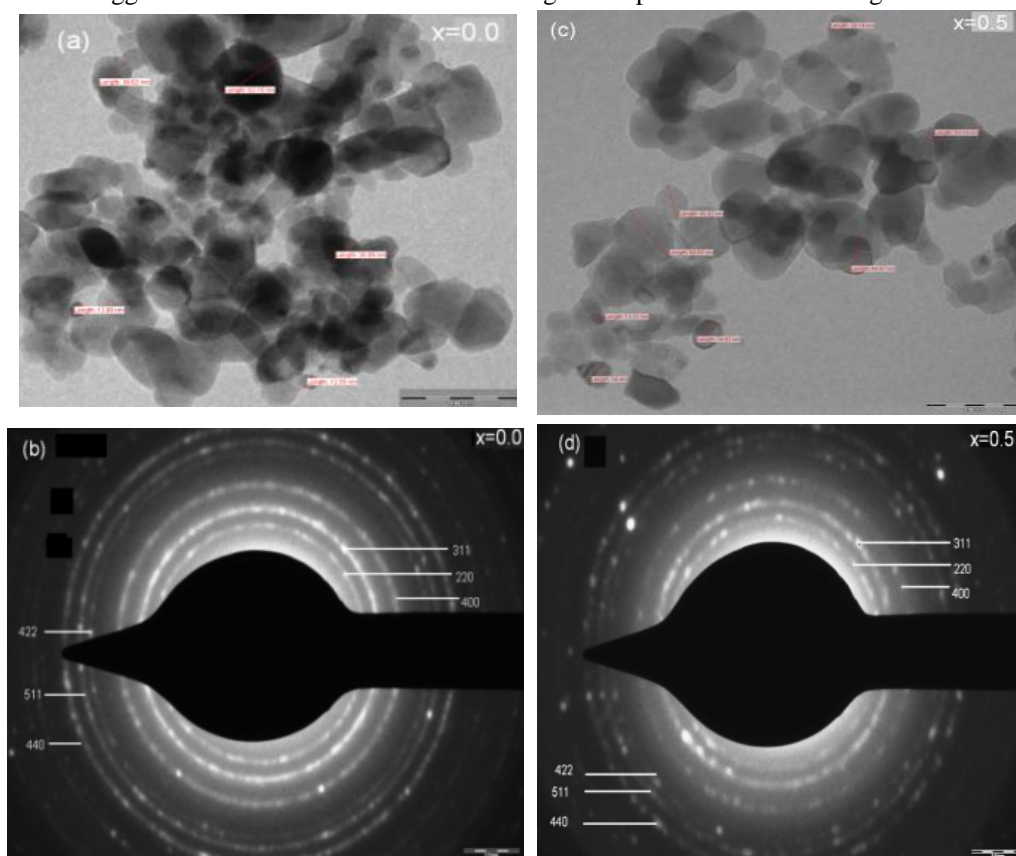


Fig.1 (a) and (c) TEM micrographs of $Ni_{0.5-x}Cu_xZn_{0.3}Mg_{0.2}Fe_2O_4$ ferrite nanopowders for $x=0$ and $x=0.5$.

Fig.1(b) and (d) SAD patterns marked with miller indices of $Ni_{0.5-x}Cu_xZn_{0.3}Mg_{0.2}Fe_2O_4$ ferrite nanopowders for $x=0$ and $x=0.5$

[9]. The estimated average particle size for $x=0$ is found to be around 34 nm and that for $x=0.5$ is found to be 41 nm. This reveals that as Cu content increases the particle size also increases. The present results suggest that, the substitution of Cu helps for the phase formation of spinel cubic lattice. It means that the temperature required for the phase formation of the ferrite with Cu doping is low as compared with undoped ferrite. One function of copper is to decrease the sintering temperature [10]. In the present case, the sintering temperature and sintering time of all the ferrite samples is same (i.e. 800 °C for 4h) even though, the Cu doped samples shows higher sized grains as compared to the remaining samples. These results suggest that, addition of Cu enhances the grain growth process, which may due to the soft nature of Cu as compared to Ni. Similar results were also observed by A. Ghasemi et al. [11] in case of Cu substituted nickel ferrite prepared by a reverse micelle process. Fig. 1 (c) and (d) shows corresponding selected-area diffraction (SAD). The diffraction patterns are composed of series of concentric circles marked with miller indices,

which show ferrite nanoparticles, which are highly polycrystalline with spinel structure. The measured average particle size is found to be in good agreement with the sizes calculated by Scherer formula.

III. ELECTRICAL PROPERTIES

I. VARIATION OF RESISTIVITY WITH TEMPERATURE

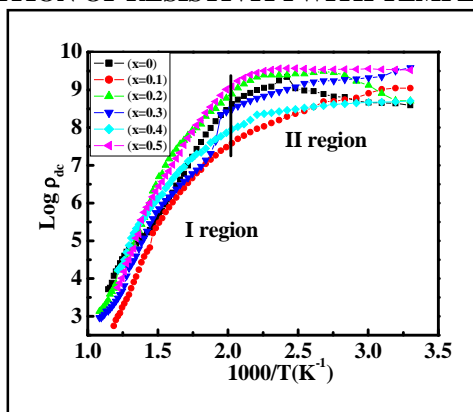


Fig.2 Variation of DC electrical resistivity with inverse temperature of ferrites samples x=0, 0.1, 0.2, 0.3, 0.4 and 0.5

Fig.2 shows variation of DC electrical resistivity with reciprocal of absolute temperature for x=0, 0.1, 0.2, 0.3, 0.4 and 0.5 ferrites samples. Fig.2 mainly shows two regions as 303K to 493K (1st region) and above 493K (2nd region). The first region is almost flat and is analogous to resistivity behavior observed for other spinel ferrites [12]. Figure 2 also indicates that all synthesized samples are semiconductor in nature. In the present case resistivity decreases with increase in temperature because conduction mechanism in polycrystalline ferrites is mainly reported to be hopping of electron between ions of the same element having different oxidation states. Under these oxidizing states, the tendency of Cu²⁺ ions formation is at octahedral site so that, some Fe²⁺ ions can be formed in ferrite in order to increase the hopping probability between the electrons. As the sintering temperature increases, more Cu⁺ ions are oxidized to Cu²⁺ ions and result decrease in resistivity with increase in temperature. The conductivity is commonly attributed to the presence of Fe²⁺ ions [13]. The conductivity arises due to the mobility of extra electron which comes from Fe²⁺ ions through crystal lattice. Similar observations were reported in case of DC conductivity of nanoparticles of Ni-Zn Fe₂O₄ ferrites [14].

II COMPOSITIONAL VARIATION OF RESISTIVITY AT ROOM TEMPERATURE

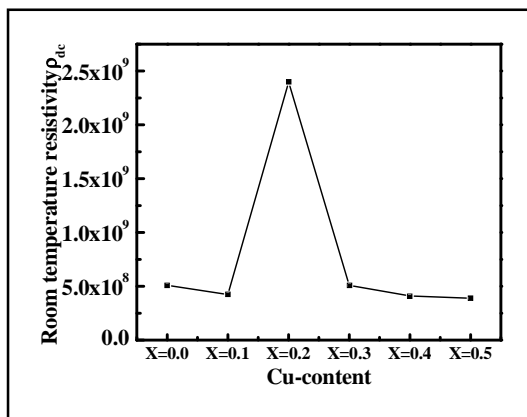


Fig. 3 Room temperature variation of DC electrical resistivity with Cu-content

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 5, May 2016

Variation of room temperature DC electrical resistivity with Cu-contents is shown in fig 3. It is revealed that as the Cu-content increases, the room temperature resistivity decreases due to the difference in grain size. Decrease in DC electrical resistivity is also attributed to increase in grain size. Smaller grains mean less grain to grain contact, which reduces the electron flow. As the grain size increase (with increase in Cu-content) resistivity is found to decrease. The room temperature DC resistivity of Mg-Cu-Zn ferrite for (x=0.1) is found to be order of $10^9 \Omega \text{ cm}$, which is much higher than that of Mg-Cu-Zn ferrite ($10^3 \Omega \text{ cm}$) prepared by the conventional ceramic method [15]. In present case the room-temperature DC electrical resistivity all of synthesised ferrites samples is found to be of the order of $10^9 \Omega \text{ cm}$ which is much higher than that of Ni-Cu-Zn ferrites ($10^7 \Omega \text{ cm}$) prepared by the conventional ceramic method [16]. From fig 3 sharp increase in resistivity at room temperature for x=0.2 may be due to the addition of Cu^{2+} and Ni^{2+} ions in place of Fe^{2+} . This will dilute the electron exchange between $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ and also hinder the electron hopping. Similar behavior is observed in Copper and Titanium-Co-doped in Copper-Zinc ferrite [17].

III. DETERMINATION OF ACTIVATION ENERGY

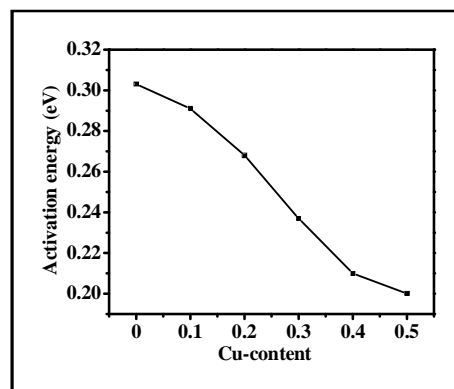


Fig 4. Variation of activation energy (in paramagnetic region) with Cu-content

Variation of activation energy in the paramagnetic region with Cu-content is as shown in fig. 4. The activation energy of each sample was determined by slope of the linear plots of DC electrical resistivity with temperature. It can be seen that, the activation energy of the dipole (in paramagnetic region) is 0.303 eV for the pristine samples whereas the value of activation energy decreases gradually as the concentration of Cu increases. For x = 0.5 the activation energy is found to be 0.2 eV. The conductivity of the samples depends upon the value of the activation energy, higher is the activation energy, means lower is the conductivity. The conductivity of the specimen increases with increasing copper content. Similar results were observed from AC conductivity measurements. The value of activation energy ranges from 0.303 to 0.20 eV. It confirms that our samples are n type conduction [18,19]. The decrease in activation energy with increase in concentration of Cu is based on change in ionic distance in the spinel ferrites. The activation energy in ferrimagnetic region is less as compared to that of activation energy in paramagnetic region. (as shown in Table1) This is because ferrimagnetic state is an ordered state; while paramagnetic state is disordered. The later requires more energy for the activation of the charge carriers. Mathe et al. [20] have discussed the anomalous behavior of activation energy in the temperature range (300 to 833K) and observed that as the temperature increases the activation energy increases from 0.15 to 0.82 eV. In the present case decrease in the activation energy may be attributed to the creation of less number of cations and development of oxygen vacancies which might become productive on rise in temperature.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 5, May 2016

Table 1 Data on variation of Cu-content (x) mole, DC electrical resistivity (ρ_{DC}), drift mobility (μ_d), activation energy in ferrimagnetic region (ΔE_1), activation energy in paramagnetic region (ΔE_2), difference between activation energy of paramagnetic region and ferrimagnetic region (ΔE), of $Ni_{0.5-x} Cu_x Zn_{0.3} Mg_{0.2} Fe_2 O_4$ ferrite samples (where $x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5) with Cu- content.

Cu-content (x)	DC electrical resistivity, (ρ_{DC}) $\times 10^8$ (Ω cm)	Drift mobility, (μ_d) (cm^2/Vs)	Activation energy		$\Delta E = \Delta E_1 - \Delta E_2$ (eV)
			Ferri region ΔE_1 (eV)	Para region ΔE_2 (eV)	
0	5.1	8.2×10^{-15}	0.118	0.303	0.185
0.1	4.2	9.7×10^{-15}	0.147	0.291	0.144
0.2	23.9	1.86×10^{-15}	0.068	0.26	0.196
0.3	5.0	7.6×10^{-15}	0.018	0.237	0.219
0.4	4.1	1.01×10^{-14}	0.134	0.21	0.076
0.5	3.9	1.1×10^{-14}	0.138	0.20	0.062

The values of DC electrical resistivity drift mobility, activation energy in ferrimagnetic and paramagnetic region difference between them are presented in Table 1. It concludes that due to high resistivity in the order of $10^8 \Omega$ cm wide applications in telecommunication. Drift mobility and activation energy give information of conduction mechanism. The present values of activation energy in the Table 1 suggest that the hopping of small polarons is responsible for the conduction in samples.

IV. DETERMINATION OF JUMP LENGTH

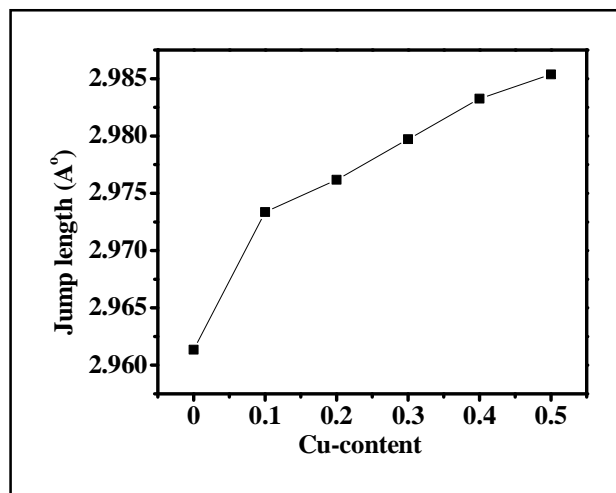


Fig. 5 Variation of jump length (L) with copper content (x)

Variation of jump length (L) is plotted as a function of copper content (x) in Fig. 5 This shows that L increases with increase in copper content. The observed increase in L with Cu-content suggests that charge carriers require more energy to jump from one cationic site to other, which causes an increase in resistivity with increasing Cu-content. The present result shows that variation of DC resistivity decrease with increasing Cu-content. This is rather expected, because of the replacement of diamagnetic Cu^{2+} ions by magnetic Ni^{2+} ion which take part in conduction process.

V.DETERMINATION OF DRIFT MOBILITY (μ_d)

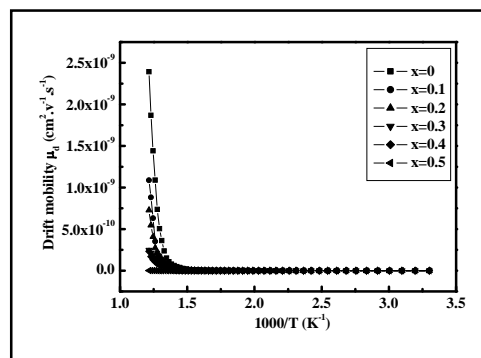


Fig. 6 Variation of drift mobility (μ_d) with temperature

The drift mobility of samples was calculated using Equation (1, 2 and 3) and is plotted as a function of inverse temperature (Fig. 6).It is observed from the plot that drift mobility remains constant during the temperature range 303 K to 733 K this is because of charge carries don't have enough energy to start hopping. As temperature increases above 733 K the charge carriers start hopping from one site to another. Drift mobility of ions is less for $x=0$ than $x=0.5$. This concludes that drift mobility increases with increase in Cu-content. The temperature variation of resistivity in this case was mainly attributed to change in drift mobility with temperature rather than to the variation of charge carrier concentration. According to the hopping model electrons are strongly localized. The localization may be attributed to electron phonon interaction. Additional localization of electrons at Fe^{2+} ions is over octahedral site in the spinel lattice. Similar results were obtained in case of Zn-Mg-Co ferrites [21].

IV. CONCLUSIONS

The auto-combustion method is found to be convenient for the synthesis of nanocrystalline Ni-Cu ferrites. The formation of single-phase cubic spinel ferrites was confirmed by SAD diffraction patterns. TEM micrographs confirm that the particles are in nanometer range. DC electrical resistivity has been explained according to site's preferences. Resultshows the compositional stability and quality of the ferrites prepared by the auto-combustion method. The conductivity of the specimen increases with increasing copper content.

V.ACKNOWLEDGMENT

Authors are thankful to U.G.C., WRO Pune for the financial support and gratefully acknowledge to Dr. V. L. Mathe, Department of Physics, University of Pune, for providing the dielectric measurement facilities and Principal T.N. Golap. SharadchandraPawarMahavidhyalaya, Lonand for his encouragement.

REFERENCES

- [1] R. G.Kharabe., R. C. Daven., C. M. Kanamadi., and B. K. Chougule., "Dielectric properties of mixed Li-Ni-Cd ferrites", SmartMaterialStructure, Vol.15,pp.N36-N39, 2006.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 5, May 2016

- [2] S. A. Uzma Ghazanfar., and G. A. Siddiqi., “Structural analysis of the Mn–Zn ferrites using XRD technique”, Materials Science and Engineering B, Vol.118, pp.84–86, 2005.
- [3] M. Guyot., “DC and low frequency conductivity of Ni-ferrite and influence of microstructure”, Journal of Magnetism Magnetic Materials, Vol.18, pp.925-926, 1980.
- [4] S. Yan., J. Yin., E. Zhou., “Study on the synthesis of Ni-Zn-Cu ferrite nanoparticles by PVA sol–gel method and their magnetic properties”, Journal of Alloys and Compounds, Vol.450, pp.417–420, 2008.
- [5] P. Dutta., M. S. Seehra., S. Thota., and J. Kumar., “A comparative study of the magnetic properties of bulk and nanocrystalline Co_3O_4 ”, Journal of Physics Condense Matter, Vol.20, pp.417-420, 2008.
- [6] P. Tartaj., “Current. Nanoscience” Nanomagnets-From Fundamental Physics to Biomedicine, Vol.2, pp.43-55, 2006.
- [7] M. H. Kryder., E. C. Gage., T. W. Mcdaniel., W. A. Challener., R.E. Rottmayer., G. P. Ju., Y.T. Hsia., and M. F. Erden, “Heat Assisted Magnetic Recording”, Proceeding of IEEE, Vol.96, pp.1810-1835, 2008.
- [8] M.R. Bhandare., H.V. Jamadar., A.T. Pathan., B. K. Chougule., and A. M. Shaikh., “Dielectric properties of Cu-substituted $\text{Ni}_{0.5-x}\text{Zn}_{0.3}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$ ferrites”, Journal of Alloys and Compounds, Vol.509, pp.L113–L118, 2011.
- [9] L. Li., C. Xiang., X. Liang., and B. Hao., “ $\text{Zn}_{0.6}\text{Cu}_{0.4}\text{Cr}_{0.5}\text{Fe}_{1.46}\text{Sm}_{0.04}\text{O}_4$ ferrite and its Nano-composites with polyaniline and polypyrrole Preparation and electromagnetic properties”, Synthetic Metals, Vol.160, pp. 28-34, 2010.
- [10] J. J. Shrotri., S. D. Kulkarni., C. E. Deshpande., A. Mitra., S. R. Sainkar., P. S. Anil Kumar., and S. K. Date., “Effect of Cu substitution on the magnetic and electrical properties of Ni–Zn ferrite synthesized by soft chemical method”, Material Chemistry and Physics, Vol.59, pp.1-5, 1999.
- [11] A. Ghasemi., E. Ghasemi., and E. Paimozd., “Influence of copper cations on the magnetic properties of NiCuZn ferrite nanoparticles”, Journal of Magnetism Magnetic Materials, Vol.323, pp.1541-1545, 2011.
- [12] M. M. Mallapur., P. A. Shaikh., R. C. Kamble., H. V. Jamadar., P. U. Mahamuni., and B. K. Chougule., “Structural and electrical properties of nanocrystalline cobalt substituted Nickel Zinc ferrite”, Journal of Alloys and Compounds, Vol.479, pp.797-802, 2009.
- [13] B. Viswanathan and V. R. K. Murthy, “Ferrite Materials Science and Technology”, Narosa Publishing House, 1990.
- [14] S. A. Saafan., T.M. Meaz., and E. H. El Ghazzawy., “Study of DC conductivity and relative magnetic permeability of nanoparticle $\text{NiZnFe}_2\text{O}_4/\text{PPY}$ composites” Journal of Magnetism Magnetic Materials, Vol.323, pp.1517-1524, 2011.
- [15] M. M. Haque., M. Huq., and M. A. Hakim., “Densification, magnetic and dielectric behaviour of Cu-substituted Mg–Zn ferrites” Material Chemistry and Physics, Vol.112, pp.580-586, 2008.
- [16] P. A. Jadhav., R. S. Devan., Y. D. Kolekar., and B. K. Chougule., “Structural, electrical and magnetic characterizations of Ni–Cu–Zn ferrite synthesized by citrate precursor method.” Journal Physics Chemistry Solid, Vol.70, pp.396-400, 2009.
- [17] H. Hsiang., L. Mei., C. H. Liu., and F. S. Yen., “Electrical properties of low temperature sintered copper and titanium-co-doped copper zinc ferrites.” Journal Alloys and Compounds, Vol.502, pp.163-168, 2010.
- [18] R. C. Kamble., P. A. Shaikh., S. S. Kamble., and Y. D. Kolekar., “Effect of cobalt substitution on structural, magnetic and electric properties of nickel ferrite” Journal of Alloys Compounds. Vol.478, pp.599-603, 2009.
- [19] R. C. Kamble., N. R. Adhate., B. K. Chougule., and Y. D. Kolekar., “Magnetic and dielectric properties of mixed spinel Ni-Zn ferrites synthesized by citrate- nitrate combustion method” Journal of Alloys and Compounds, Vol.491, pp.372-377, 2010.
- [20] V. L. Mathe., and R. B. Kamble., “Anomalies in electrical and dielectric properties of nanocrystalline Ni-Co spinel ferrites” Material Research Bulletin Vol.43, pp.2160-2165, 2008.
- [21] M. J. Iqbal., and M. R. Siddiquah., “Structural electrical and magnetic properties of Zr-Mg cobalt ferrite” Journal of Magnetism Magnetic Materials, Vol.320, pp. 845-850, 2008.