JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 17, No. 7-8, July – August 2015, p. 1075 - 1079

Structural, dc resistivity and activation energy studies of NiCuZn ferrite

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Copper substituted Nickel-Zinc ferrite composition of $Ni_{0.7-x}Zn_{0.3}Cu_xFe_2O_4$ prepared by conventional ceramic method. The single phase cubic structures of the samples were confirmed from X-ray diffraction patterns. The average Grain sizes of the sintered samples are also studied with doping concentrations. Electrical properties namely DC-resistivity as a function of temperature were studied for ferrite samples. Log of resistivity also studied as a function of $1/\text{ T k}^{-1}$. Conduction mechanism studied with Activation energy as a function of concentration on the basis of Verwey's hopping mechanism.

(Received December 16, 2013; accepted June 24, 2015)

Keywords: Ferrites, Ceramic, Electron hopping, dc-resistivity, Activation energy. Verwey's hopping mechanism

1. Introduction

Ni-Zn ferrites are most versatile electronic ceramic materials suited for high frequency application in the telecommunication field [1]. Ni-Zn ferrites show good magnetic properties for technical applications [2]. The interesting physical and chemical properties of ferrospinal depend upon the method of preparation [3], site preference of cation among the available tetrahedral (A) site and octahedral (B) site. Nickel ferrite is an inverse spinel, where as Zinc ferrite is a normal spinel. Hence it is interesting to study Ni-Zn ferrites are soft magnetic materials for high frequency applications. These ferrites are used in radio frequency circuits, high quality filters, rod antennas, transformers core, read/write heads for high speed digital tape and operating devices [4]. The study of electrical resistivity produces valuable information on the behavior of free and localized electric charge carried in the studied samples. The electrical resistivity of Ni-Zn ferrites processed through conventional ceramic technique was studied as function of temperature; the activation energy was also studied with copper concentration. Cu is conventionally used in NiCuZn ferrite to improve densification as well as electromagnetic properties [5]. The beneficial effect of copper ions on the densification of ferrite can be reasonably explained by possible sintering mechanisms that take place through a high atomic mobility of Cu ions at relatively less than the average intensity of heat. During the sintering process diffusion [6] at grain boundary increasing the grain growth owing to lesser grain boundary than the activation energy for lattice diffusion. Cu is used in this ferrite to decrease the sintering temperature. However, Cu decreases the resistivity of the ferrite, which is not desirable for its high frequency applications. So, most effective use of Cu content with respect to densification and resistivity of the ferrites are very important.

2. Experimental details

Ni-Zn ferrite of composition $Ni_{0.7-x}Zn_{0.3}Cu_xFe_2O_4$ (x=0.00 to 0.50 in the steps of 0.05) were prepared by conventional ceramic technique, using A.R. grade NiO, ZnO, Cu_2O, and Fe_2O_3 compounds with high purity. They were mixed in their stoichiometric proportion, ground methanol base agate motor about four hours to get fine powder the pre-sintering powders was carried out at 850 °C for 4 hours in the muffle furnace, samples were allowed to cool by natural process. These calcined powders then pressed into cylindrical shape pellets of desired thickness with the help of hydraulic press by applying three tones for four minutes. Further these pellets were finally sintered at 1100 °C for four hours staying temperature, cooled by natural process. The phase purity of the samples was analyzed by using the X-ray diffraction method with cu-$k_{\acute{\alpha}}$ radiation. The DC resistivities of all the samples were measured by two probe method in the temperature range 303K-553K. The Verweys hopping transition mechanism is discussing with the help of activation energy.

3. Results and discussions

Xrd and SEM studies are two most important techniques to study crystal structure and microstructure of ferrites respectively. Sintering is one of the critical steps in the development of microstructures. Density and improvement of grain size occur at the same time during the sintering process, increase in grain size and a change in pore shape. The microstructures developed at various stages of sintering are determined by the sintering kinetics [7], the study of sintering kinetics is thus useful in understanding various properties of the product so obtained.

X-ray diffraction technique is widely used for determining the atomic spacing from the observed diffraction angles. For a given set of planes (hkl), the spacing (d) is given by

$$d_{hkl} = n\lambda/2\sin\theta$$

where n is the order of reflection,
λ is the wavelength of radiation, and
θ is the glancing angle of incidence of x-ray beam.

The lattice constant (a) of the ferrite can be calculated using the relation

$$a = d / (h^2+k^2+l^2)1/2$$

X-ray patterns for all the ferrite samples in this study have been obtained on a Siefert x-ray diffractometer. All the patterns exhibit lines corresponding to single phase spinel structure with cubic symmetry. Typical X-ray patterns for samples Ni-Cu-Zn Ferrites are shown fig.1. The phase formation behavior was studied by X-rd. Fig.1, shows the X-rd patterns of sintered powders. Accurate determination of lattice constant has been obtained from the extrapolation of calculated lattice constant against Nelson-Riley function [8] for which the function is zero. X-ray diffraction patterns, single phase spinel structure indicating the solubility of cations into their respective lattice sites. A monatomic increase in lattice constant fig.2 is observed with increasing copper concentration. This variation is accordance with Vegard’s law [9], which states that in a solid solution of spinels with in the ability range, a linear change in lattice constants with the concentration of components is observed. The typical lattice constant is starts from 8.3785 to 8.4384 and this increase in lattice constant is expected in view of the fact that the ionic radius of substituted Cu^{2+} ion (0.72 A^0) is larger than the displaced Ni^{2+} ion (0.69A^0). Ferrites prepared by a correct ceramic technique will have a single phase with definite grains and grain boundaries. Scanning electron microscope is one of the important tools that can give information regarding the microstructure of the solid sample. SEM works on the principle that when narrow focused beam of electrons sweeps over the material, the scattered electrons interact with the atoms of the materials. This results in release of secondary electrons such as Auger electrons and emission of characteristic X-rays. The image of ferrite material surface is usually formed by the secondary electrons of low energies. Fig.3 shows the typical SEM images of the sintered ferrite samples. From the SEM images, the grain size can be obtained as given below [10],

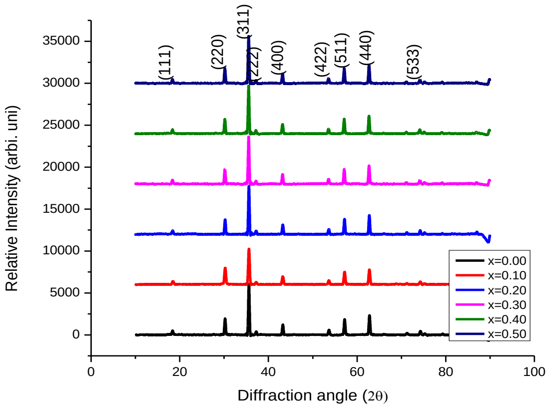


Fig.1. Shows the typical xrd spectrum of NiCuZn.

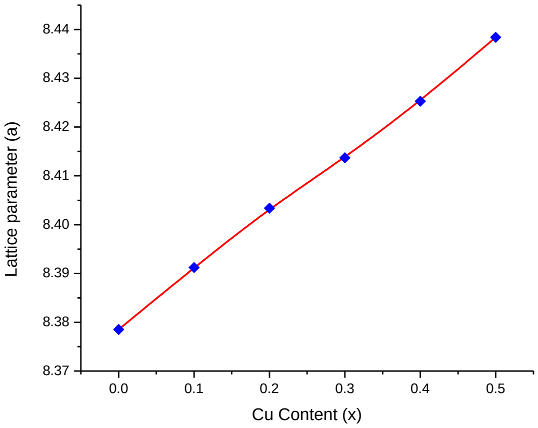
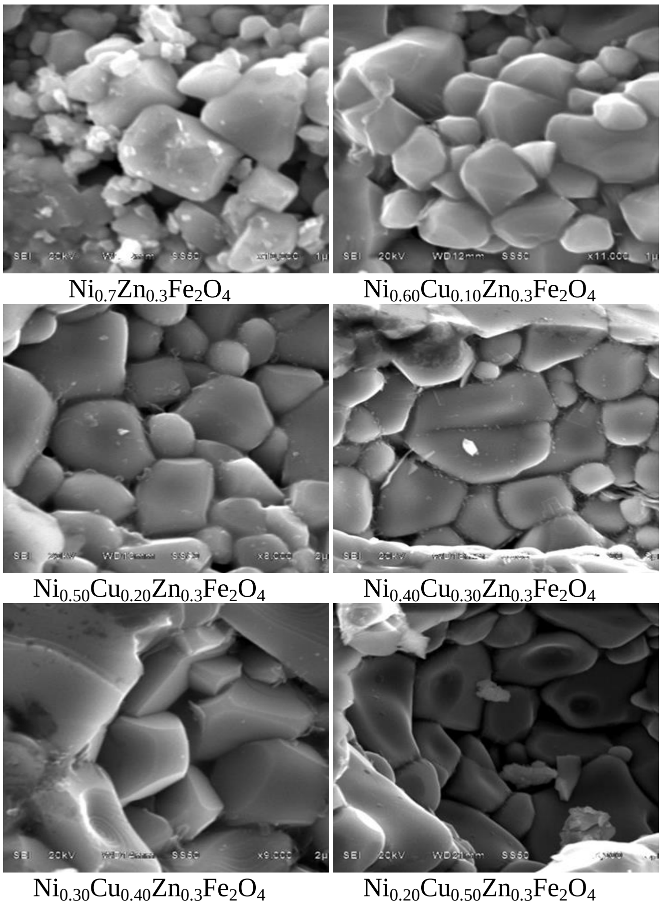


Fig.2. Shows the typical lattice constant with cu.

$$D^2m = S/l^2n$$

Where S is the Area of a section of micrograph, l indicates the linear magnification & n is number of grains in the section.



$Ni_{0.7}Zn_{0.3}Fe_2O_4$ $Ni_{0.60}Cu_{0.10}Zn_{0.3}Fe_2O_4$

$Ni_{0.50}Cu_{0.20}Zn_{0.3}Fe_2O_4$ $Ni_{0.40}Cu_{0.30}Zn_{0.3}Fe_2O_4$

$Ni_{0.30}Cu_{0.40}Zn_{0.3}Fe_2O_4$ $Ni_{0.20}Cu_{0.50}Zn_{0.3}Fe_2O_4$

Fig.3. Shows the typical SEM images of the $Ni_{0.7-x}Zn_{0.3}Cu_xFe_2O_4$.

The purpose of sintering in ferrite preparation is to increase the density due to the inter diffusion of the constituent metal ions occupying the vacancy positions in the material with respect to grain growth. The sintering process with respect to grain growth can be divided into three stages [11]. a) Initial stage of no grain growth or no change in pore volume. b) Intermediate stage of grain growth and stage of pore elimination starts. c) Final stage of brisk grain growth due to faster occupation of pores. Even after reaching the end point density, grain growth will continue at higher temperatures with time [12, 13]. The vacancies are transported to grain boundaries and get sintered. As a result the pores will be filled up and density increases as log of sintering time in general.

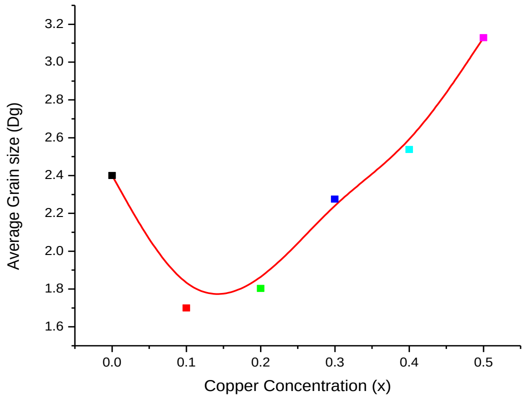


Fig.4. Shows the grain size of the typical ferrite samples with copper concentration

The grain size of the typical ferrite samples with copper concentration as shown in the Fig. 4. The grain size is found to increase with increasing the copper concentration. From the above drawn graph the ions have influenced the nature and formation of pores. It is observed that the porosity varies inversely with grain size. This means the lower the values of grain size higher will be the percentage of porosity. The grain size (2.4µm) of the basic ferrite is ($Ni_{0.7}Zn_{0.3}Fe_2O_4$). In the Ni-Zn ferrite system, the zinc ions with free 4s4p orbitals ready to form covalent bond with oxygen, predispose them to occupy tetrahedral sites, while the nickel ions due to their high crystal field stabilization prefer octahedral sites only and the iron ions are distributed among both A and B-sites

DC electrical resistivity varies with the variation in composition. The change in dc electrical resistivity can be explained on the basis of Verwey's hopping mechanism [14]. According to Verwey, the electrical conduction in ferrites is due to the hopping of electrons between the ions of same element present in different valence state at octahedral (B) site. In other words, the conduction in ferrites is mainly due to the hopping of electrons between Fe^{3+} and Fe^{2+} ions present at B-site [15]. The resistivity of a ferrite material in general, depends upon the final chemical composition of the prepared ferrite due to sintering conditions, hopping mechanism and other conduction mechanisms. By the addition/substitution of cations to a ferrite produces changes in the resistivity (ρ). Further, the cation distribution among A and B sites, change magnetic properties. One has to consider Fe^{2+} ion concentration in order to discuss about eddy current losses in connection with electrical resistivity. Fig. 5 shows the room temp. log of resistivity with Cu content.

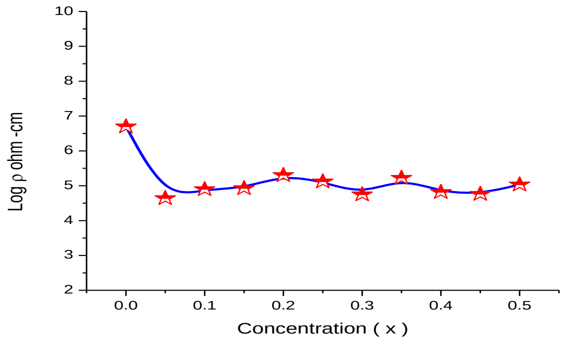


Fig. 5. Shows the variation of room temperature log of resistivity with Cu content.

Ferrites are insulators but they show semiconductor like behavior with the rise of temperature. Their resistivity varies with temperature according to Arrhenius equation [16]

$$\rho = \rho_\infty e^{\Delta E/KBT}$$

Here ρ is the resistivity at a particular temperature, ρ is the resistivity extrapolated to T = ∞, T is the absolute temperature, k_B is the Boltzmann constant and ΔE is the activation energy, which is the energy needed to release an electron from the ion for a jump to neighboring ion, cause to happen the electrical conductivity. The rise in temperature on the resistivity is that it changes the mobility of the carriers which gives rise to the hopping of charge carriers between the same lattice sites. A consequence the resistivity decreases when raise the heat and increases the conductivity.

The exchange of the electrons of the same element of the conduction mechanism in the ferrite sample can be explained on the basis of Verwey hopping transition mechanism (VHTM) [9] and are distributed randomly over crystallographically equivalent lattice sites. The conduction is due to the exchange of 3d electrons between Fe^{2+} and Fe^{3+} ions in the octahedral site. The formation of Fe^{2+} ions in tetrahedral site can be ruled out for the simple reason due to the absence of Fe^{2+} ions at A-sites and any Fe^{2+} ions formed during processing preferentially occupy B sites only. The formation of Fe^{2+} ions in the material is to satisfy the charge balance in the lattice. Creation of Fe^{2+} ions gives raise the transfer of electron between the Fe^{3+} and Fe^{2+} ionic states. The loss of zinc leads to the formation of ferrous ions in the lattice and thereby increases the conductivity. In the present study, as the samples are sintered at 1100 °C loss of zinc from the material is expected which further creates pores in the material. Because of these pores, dc resistivity of the material increases. But copper act as a sintering aid and copper forms liquid phase at the grain boundary hence substitution copper leads to an increase in conductivity through grains in the material. Therefore a decrease in resistivity has to be observed with increasing Cu concentration. Similar tendency has been noticed in the current study. As expected in semiconductors, the observed dc resistivity falls exponentially with increasing temperature for all these compositions. Activation energies for all the samples have been determined from the slope of log of resistivity (log ρ) versus reciprocal of absolute temperature (1/T) plots and are shown in fig.6.

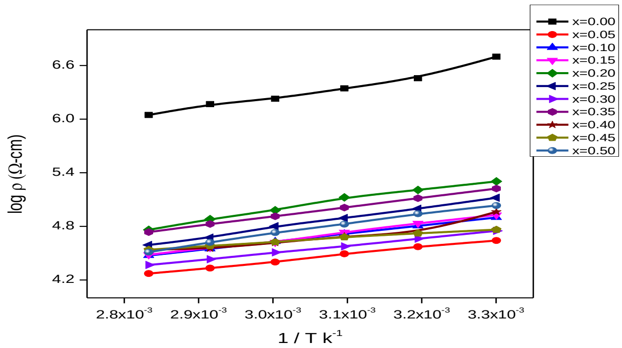


Fig. 6. Shows variation of the temperature dependence the log of resistivity.

In ferrites, electrical energy is defined as the energy needed to release an electron from the ion for a jump to the neighboring ion, so giving rise to the electrical conductivity. The activation energy decreases with the increase in temperature. This is due to the increase in concentration of Fe^{2+} ion with the rise in temperature. Fe^{2+} ions cause more diffusion of electrons and leads to the reduction in activation energy. In general, in ferrites, the activation energy is decided by the hopping probability of electrons among $Fe^{3+} \leftrightarrow Fe^{2+}$. Fig. 7 shows the activation energies with copper concentrations, a similar tendency that of compositional dependency of dc resistivity of the material. Activation energies showed in the range of 0.1442 eV to 0.2852 eV which represents hopping between the electrons among $Fe^{3+} \leftrightarrow Fe^{2}$.

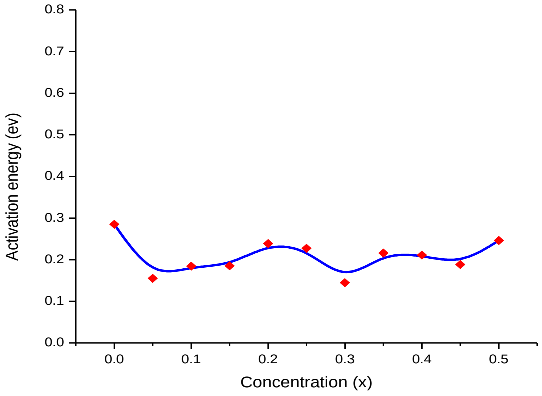


Fig. 7. Shows the variation of the activation energy with Cu content.

4. Conclusions

The typical ferrite samples of the Cu substituted Ni-Zn ferrite prepared by the conventional ceramic technique. Xrd patterns confirm the single phase cubic spinel. The powders were in crystalline state and identification revealed spinel ferrite phases similar to JCPDS card number 48-0489. The lattice constant (a) is increases with increasing the doping concentration (x) due to zinc ions occupy Tetrahedral-site, Ni ions preferred for Octahedral-site, when Cu replace in Ni at Octahedral B-site then the lattice constant increases, the Cu ionic radius is larger than compared Ni ionic radius. The grain size increases with the rise in Cu substitution. The sintering temperature of all the samples is 1100 °C; this may be influence the grain size. The dc electrical resistivity gives information about the internal electrical charge carriers of the ferrite samples. In the cu substituted Ni-Zn ferrite the sintering process may plays a crucial role in microstructure and resistivity. The variation in resistivity has been interpreted in terms of the contributions arise from the loss of zinc leads to the formation of ferrous ions in the lattice and thereby increases the conductivity and decreases the resistivity. The activation energy decreases with the increase in temperature. This is due to the increase in concentration of Fe^{2+} ion with the rise in temperature. Fe^{2+} ions cause more diffusion of electrons and leads to the reduction in activation energy. Activation energies varies from 0.1442 eV to 0.2852 eV which represents hopping between the electrons among $Fe^{3+} \leftrightarrow Fe^{2+}$.

Acknowledgements

This work has been financially supported by UGC-BSR Fellowship, MHRD. India.

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