

Structural Observations, Density and Porosity Studies of Cu Substituted Ni-Zn Ferrite through Standard Ceramic Technique

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Abstract: Polycrystalline NiCuZn ferrites prepared by solid state reaction method with various concentrations of copper generalized as $\text{Ni}_{0.7-x}\text{Cu}_x\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ with the x varying from 0 to 0.50 in steps of 0.05 variations. In this paper we present the structural, density and porosity. The powders of the samples were used to characterize the x-ray diffraction. The XRD patterns of the samples provide the evidence of the single cubic crystal symmetry phase. The microstructure of the NiCuZn ferrite average grain size is recorded by SEM. The NiCuZn ferrite system having low cost and low firing metals for preparing the multi layer ferrite chip inductors and higher densification than the Mn-Zn ferrite.

Keywords: NiCuZn, Spinel, XRD, Density

Introduction

NiCuZn ferrites are excellent soft magnetic materials in high frequency devices due to their low cost, high resistivity and low eddy current losses, which have been studied extensively for multiplayer chip inductor applications^{1,2}. But till today, NiCuZn ferrites are meant for RF integrated inductors have been reported scarcely. $\text{Ni}_{0.4}\text{Cu}_{0.2}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ thin films were fabricated by sol-gel method and RTA process. In present days the researchers have been focused on NiCuZn of the most widely used for manufacturing the multilayer ferrite chip inductors (MLCFIs), which have attracted the attention of many of them³. Structural and dielectric properties of these materials are highly sensitive to composition and preparation method. Recently much effort is being given to improve the properties of these ferrites and to understand their basic physics^{4,5}. The miniaturization trends of electronic devices resulted in the development of new device multilayer ferrite chip inductor (MLFCI) components. Materials with high permeability are required for MLCIs to develop miniaturized circuits.

Experimental

$\text{Ni}_{0.7-x}\text{Cu}_x\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ ferrite was prepared by the standard solid-state reaction method. High purity NiO, ZnO, CuO and Fe_2O_3 powders were weighed in stoichiometric proportions, the powders were grounded with agate mortar pestle with the medium of methanol for six hours, after the powder samples were calcined at 850 °C for 4 h in air atmosphere using programmable muffle furnace. Then, the powders were again grounded with 10% PVA using as a binder; powders were uniaxially compressed by pressing into toroid and cylindrical shape and sintered at 1100 °C for four hours in air atmosphere. X-ray diffractometer system (X-Pert, pro) with Cu K-Alpha (1.54060 \AA) was used to study the structure of the nature of spinel at the room temperature of all the doping and undoped ferrite specimen powders. The microstructure and grain size analysis of the samples was studied by microscopic observation of polished and etched specimens using JOEL / JSM-6610LV Scanning Electron Microscope. For morphological studies and micro-structural analysis, after thermal etching of the materials, scanning electron microscopic photographs were obtained. Densities were calculated by using the Archimedes method.

Results and Discussion

XRD-Analysis

X-ray diffraction patterns of $\text{Ni}_{0.7-x}\text{Cu}_x\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ shows single phase spinel structure in all the samples prepared. The phase formation behavior was studied by XRD. Figure 1 shows XRD patterns of shows the as-burnt ferrite powders. Miller indices (h k L) are represented for each peak in the x-ray diffraction patterns. The powders were in crystalline state and identification revealed spinel ferrite phases similar to JCPDS card number 48-0489⁶. The corresponding d-values of all the peaks found to be in agreement with that reported for Ni-Zn ferrite^{7, 8}.

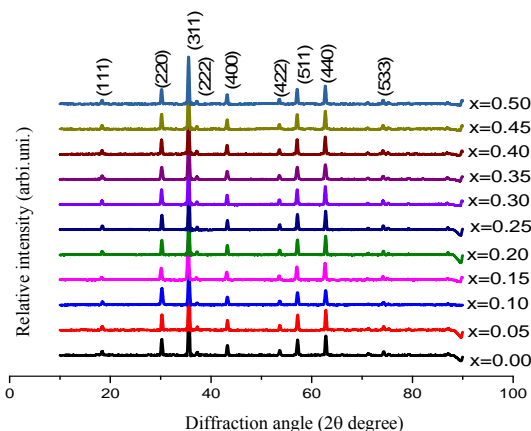


Figure 1. X-ray diffraction patterns of $\text{Ni}_{0.7-x}\text{Cu}_x\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$

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

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

All the patterns exhibit lines corresponding to single phase spinel structure with cubic symmetry. Typical For accurate lattice constant determination of the sample, a graph between the lattice constant and an error function which accounts for all possible errors that arise in the measurements of θ was plotted using Nelson-Riley function⁹ to minimize error.

A line joining the various points with emphasis on high angle points, which are $\theta = 90^\circ$ and at which the various error vanishes, was taken as the lattice. Lattice parameter was found to increase with increasing Cu substitution. In general, in Ni-Zn ferrites, Zn ions tend to occupy A-sites and Ni ions have preference for B-sites. When Cu ions replace Ni ions in B-sites, a slight increase in the lattice constant is expected because of the larger ionic radius of copper (0.69 \AA) compared to the Ni^{2+} (0.73 \AA)¹⁰. It is well known that replacement of a large ion by a small ion eventually increases the lattice constant of the ferrite lattice and the same has been noticed in the current investigation. The patterns of all the samples exhibited lines corresponding to single phase spinel structure of Ni-Zn ferrite with cubic symmetry. This is confirmed by comparison of experimental d -spacing values with the international center for diffraction data (ICDD) cards. The variation of lattice constant 'a' as a function of copper ion concentration is shown in Figure 2.

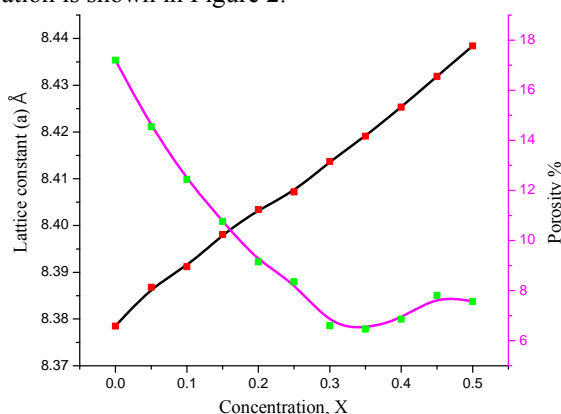


Figure 2. The variation of lattice constant and porosity as function of concentration (x)

The lattice constant increases linearly with increasing the Copper concentration, similar kind of results is observed by others¹¹⁻¹³. Sintering is a thermally activated process during which the total interfacial free energy of the ensemble of particles in the compact decreases due to mass transport. Transport of material is taken place mostly by volume diffusion of atoms and ions¹⁴. Volume diffusion proceeds either by an interstitial or by a vacancy mechanism. The porosity (P%) due to the addition intragranular porosity and intergranular porosity of the grains¹⁵. In our studies the total porosity (P%) decreases with increasing the copper concentration due to the intergranular porosity increases at higher concentrations intragranular slightly increases. The intragranular porosity depends on the sintering temperature and the intergranular porosity depends on the grain growth. At higher concentrations the porosity (P%) slightly increases at $x=0.35$ to 0.50 in steps of 0.05 variation, which arises the substituent concentration copper and it acts as sintering aid.

Microstructure observations

Figure 3 shows the scanning electron micrographs recorded for Ni-Cu-Zn ferrites. The variations in grain size (Dg) as a function of substituent concentration(x) is shown in Figure 4. A close look at the microphotographs shows the presence of pores inside the grains. As discussed above the substituted ions have influenced the nature and formation of pores. It is observed that the porosity varies inversely with the grain size, except for few cases at higher substituent concentration (x). This means lower the values of grain size, higher will be the percentage of porosity.

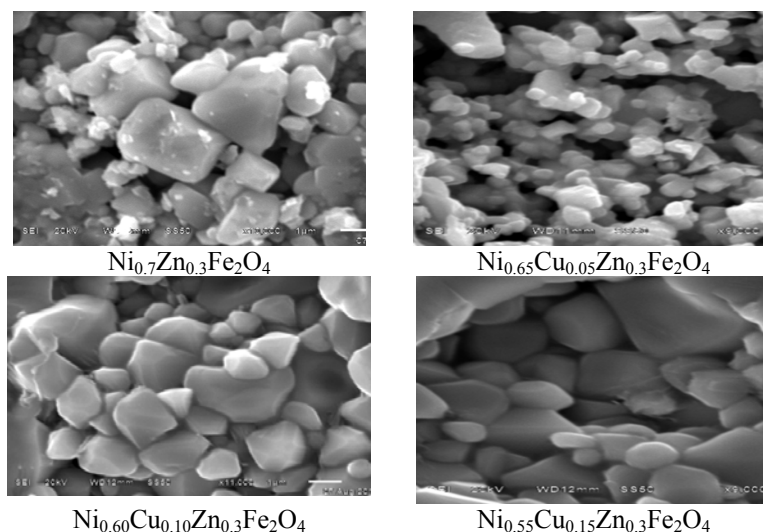


Figure 3. Typical SEM images of the $\text{Ni}_{0.7-x}\text{Cu}_x\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ ferrite system

The surface morphology of all the samples as seen from Figure 3 the SEM consists of the average grain size is varying from $0.542\ \mu\text{m}$ to $3.129\ \mu\text{m}$ as shown in the Figure 4. From the plotted figure it is observed that the average grain size increases with the rise in Cu substitution. The rate of the grain growth of the specimens influences the magnetic properties. All the specimens were sintered at $1100\ ^\circ\text{C}$, increases in grain size may be attributed to the higher atomic mobility of Cu ions and similar kind of trend reported by *Dimri, Zhen* and *yang*¹⁶⁻¹⁸. The Copper has lower melting temperature than the nickel; this can also be effect the grain size. This similar type of results agrees for Zn^{+2} and Cd^{+2} and substituted ferrite^{19,20}. The sintering temperature of all the samples is $1100\ ^\circ\text{C}$, this may be influence the grain size. The increases in density of the samples also influence the increase in grain size and decrease in the degree of porosity can be seen from the micrograph.

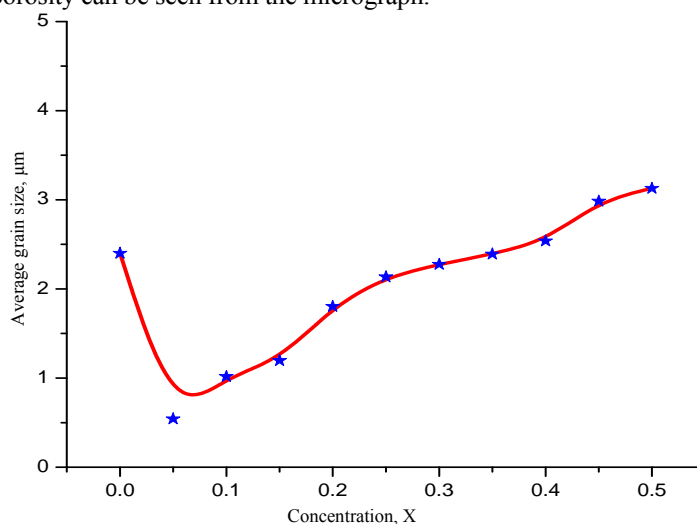


Figure 4. The variation of the average grain size (Dg) with Cu concentration

X-ray density, bulk density and porosity studies

Density (x-ray density) for each sample is calculated taking the experimentally evaluated lattice parameter 'a' by using the formula²¹.

$$\text{X-ray density} = (dx) = 8M/Na^3,$$

where 8 = Number of molecules for unit cell of a spinel lattice, M = Molecular weight in gram mole of the spinel, N = Avogadro number.

The x-ray density (dx) steadily decreases with increasing amounts of concentration. The bulk density (db) has been determined by Archimedes principle and is found to decrease with substituent concentrations up to $x=0.35$, then increases slowly at higher concentrations as shown in Figure 5. The observed bulk density 4.5552, x-ray density 5.3387 and porosity 17.2 for the basic ferrite have close agreement with the reported value sintered at 1100°C ²². The x-ray density is found to exhibit higher value when compared with its bulk density for all ferrites. The variation between them could be related to the porosity in the crystalline structure of the material. The observed porosity range from 17.2 to 6.468%²³ and indicates that the materials are high porosity. This is characteristic requirement for good quality ferrite material since larger porosity affects physical properties of the material. At higher and intermediate concentrations of substituent's the material it is found to exhibit low porosity. However it is understood that higher concentration of additive cause improvement of the quality of the material with respect to low porosity.

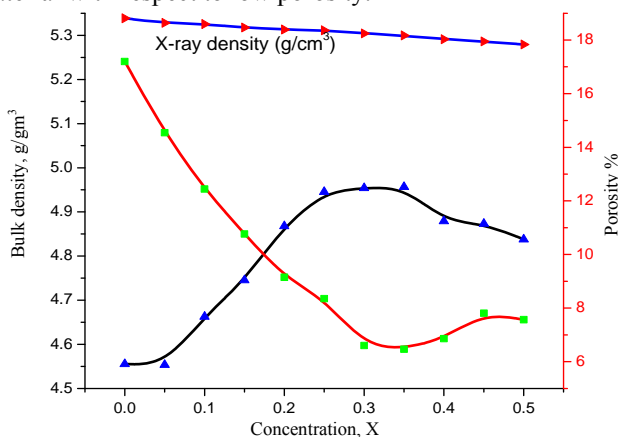


Figure 5. The variation of the x-ray, bulk densities and Porosity as a function of the Cu content

Conclusion

All the x-ray diffraction patterns and infrared spectrum exhibit lines corresponding to single phase spinel structure with cubic symmetry. Accurate determination of lattice constant has been obtained from the extrapolation of calculated lattice constant against Nelson-Riley function. Lattice parameter was found to increase with increasing Cu substitution. In general, in Ni-Zn ferrites, Zn ions tend to occupy A-sites and Ni ions have preference for B-sites. When Cu ions replace Ni ions in B-sites, a slight increase in the lattice constant is expected because of the larger ionic radius of copper (0.72 \AA) compared to the Ni^{2+} (0.69 \AA). The grain size increases with the rise in Cu substitution. The sintering temperature of all the samples is 1100°C , this may influence the grain size. The increases in density of the samples also influence the increase in grain size and decrease in the degree of porosity can be seen from the micrographs.

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