

Synthesis, Structural and Physical Properties of $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ Ferrites

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ABSTRACT

Zn substituted Cu-Zn ferrites with a composition $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ have been synthesized by standard double sintering ceramic method and characterized by X-ray diffraction. The single-phase cubic spinel structure of all the samples has been confirmed from X-ray diffraction analyses. The lattice constant is found to increase linearly with the zinc content obeying Vegard's law. This increase in lattice parameter is explained in terms of the sizes of component ions. It is well known that density plays a key role in controlling the properties of polycrystalline ferrites. The X-ray and bulk densities of the Cu-Zn ferrite is significantly decreased whereas porosity increased with increasing Zn concentration, thereby giving an impression that zinc might be helping in the densification of the materials. SEM micrographs exhibit a decrease in grain size with increasing Zn content. The real part of initial permeability, μ' increase with increasing Zn contents upto $x = 0.5$ after that it decreases with higher Zn content.

Keywords: Ferrites, XRD, Lattice Parameter, Density, Porosity, Permeability

1. Introduction

Ferrites, i.e. ferrimagnetic cubic spinels, possess the combined properties of magnetic materials and insulators. Ferrites represent an important class of functional magnetic materials, largely used in electronic industry and many other fields of interest, like high frequency devices, solid state physics, mobile communications of information technology [1-3]. By virtue of their magnetic and semiconducting properties the copper ferrite and its solid solutions with other ferrites are employed as magnetic materials for multilayer chip inductors but also for transducers of high thermomagnetic sensitivity [4,5]. The copper ferrite has the structure of the mineral spinel corresponding to the general chemical formula MeFe_2O_4 where Me is Cu or a divalent ion of the transition elements and Fe is the iron trivalent ion Fe^{3+} . As long as the ions are distributed in this way over A (tetrahedral) and B (octahedral) position the spinel is known as normal. When divalent ions are distributed on B position and trivalent ones on A position the spinel is known as inverse. For instance zinc ferrite is normal and copper ferrite completely inverse and these are extreme cases. In reality there is a random distribution of the ions over A

and B sites and each composition is characterized by a degree of inversion, which very much depend on the preparation. Mixed ferrites have different degrees of inversion and CuZn ferrites proved to be very sensitive to thermal treatments having different cation distribution upon annealing and mainly upon cooling speed from high temperatures. The objective of this work is to synthesize the Zn substituted Cu-Zn ferrites and to investigate the effect of zinc ions which substitute iron in ferrite, on the structural and physical properties of Cu-Zn ferrite by studying XRD, SEM and frequency dependence permeability.

2. Materials and Method

Ferrite samples of the chemical formula $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7$) were prepared by the double sintering ceramic technique. High purity reagent powders of CuO, ZnO, and Fe_2O_3 were dried at 150°C and were weighed precisely according to their molecular weight. Intimate mixing for the materials was carried out for 4 hours using agate mortar and then the materials in ethyl alcohol are poured into an agate jar with two types of stainless steel balls of different sizes.

The weight ratio of material to ball was 1:5 under air atmosphere. The jar was placed into a planetary grinding miller, and then the materials were continuously milled for 4 hours. The slurry was dried and was pressed into disc shape sample. The disc shaped sample was pre-sintered at 850°C for 6 hours at a heating rate of $4^\circ\text{C}/\text{minute}$ in air to form ferrite through chemical reaction and then cooled down to room temperature at the same rate as that of heating. The pre-sintered material was again crushed and wet milled for another 4 hours in distilled water to reduce it to small crystallites of uniform size. The mixture was dried and a few drops of saturated solution of polyvinyl alcohol were added as a binder.

The resulting powders were pressed uniaxially under a pressure of (20 Pa) in a stainless steel dies to make pellets. The pressed pellets (9 mm diameter, 3 mm thickness) toroids (12 mm outer diameter, 8 mm inner diameter and 4 mm thickness) were then finally sintered at 950°C for 4 hours in air and cooled in the furnace. All samples were heated slowly in the programmable Muffle furnace (Model HTL 10/17, Germany) at the rate of about $220^\circ/\text{hours}$ increase to avoid cracking of the samples. Then, the temperature was raised to firing temperature of 950°C and kept at this temperature for 4 hours. The surfaces of all the samples were polished in order to remove any oxide layer formed during the process of sintering. The weight and dimensions of the pellets were measured to determine bulk densities. Phase analysis was done by X-ray diffraction using Phillips (PW3040) X' Pert PRO X-ray diffractometer. The powder specimens were exposed to CuK_α radiation with a primary beam of 40 kV and 30 mA with a sampling pitch of 0.02° and time for each step data collection was 1.0 sec to characterize it. A 2θ scan was taken from 10° to 90° to set possible fundamental peaks where Ni filter was used to reduce CuK_β radiation. All the data of the samples were analyzed using computer software "X' PERT HIGHSCORE". X-ray diffraction patterns were carried out to confirm the crystal structure, where no extra lines were found indicating the absence of the starting oxides or any other phases. The microstructures of the samples were done by a scanning electron microscope (SEM) (model: FEI Inspect). The SEM micrographs were taken on the smooth surface of the pellet-shaped polished samples. Before taking micrographs, the surface of the samples were thermally etched at a temperature of 150°C below the sintering temperature. Frequency dependence initial permeability of the toroid shaped samples was measured with 6500B impedance analyzer at frequency range upto 15 MHz.

3. Results and Discussion

The structural study is essential for optimizing the properties needed for various applications. The phase identification and lattice constant determination were performed

on an X-ray diffractometer. The X-ray diffraction patterns of the synthesized Zn substituted mixed ferrite $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ is shown in **Figure 1**. All the samples show good crystallization, with well-defined diffraction lines. Powder X-ray diffraction of the ferrite samples, showing well-defined reflections without any ambiguity, reveals the formation of single-phase cubic spinel structure and all the peaks observed match well with those of Mg-Cu-Zn, Mg-Cu and Zn-Mg ferrites reported earlier [6-8]. The X-ray lines show considerable broadening, indicating the fine particle nature of the ferrite powder. It is obvious that the characteristic peaks for spinel Cu-Zn ferrites appear in all samples as the main crystalline phase. The peaks (220), (311), (222), (400), (422), (511) and (440) correspond to spinel phase. A strong diffraction from the planes (311), (511) and (440) as well as weak diffraction from the planes (220), (222), (400) and (422) appeared in the X-ray diffractograms. Generally, for the spinel ferrites the peak intensity depends on the concentration of magnetic ions in the lattice.

After that, using the X-ray data, the lattice constant (a_0) and hence the X-ray densities were calculated. The lattice constant was determined through the Nelson-Riley extrapolation method. The values of the lattice constant obtained from each reflected plane are plotted against Nelson-Riley function [9]

$F(\theta) = 1/2 [\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta]$, where θ is the Bragg's angle and straight lines are obtained as shown in **Figure 2**. The accurate values of lattice constant, a_0 were estimated from the extrapolation of these lines to $F(\theta) = 0$ or $\theta = 90^\circ$.

Figure 3 shows the variation of lattice constant with Zn concentration. A linear increase was evidenced in the lattice constant with increasing Zn^{2+} ion concentration from 8.365 \AA for Cu-Zn ferrite for $x = 0.0$ to 8.439 \AA for $x = 0.7$. The increase in lattice constant with content of Zinc indicates that the present system obeys the Vegard's law [10]. An increase in lattice constant with an increase in the content of Zn can be attributed to the ionic size differences since the unit cell has to expand when substituted by ions with large ionic size. Since the ionic

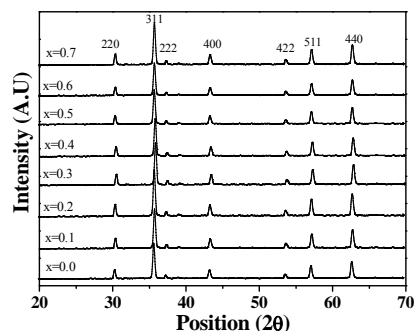


Figure 1. XRD pattern of $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0 - 0.7$).

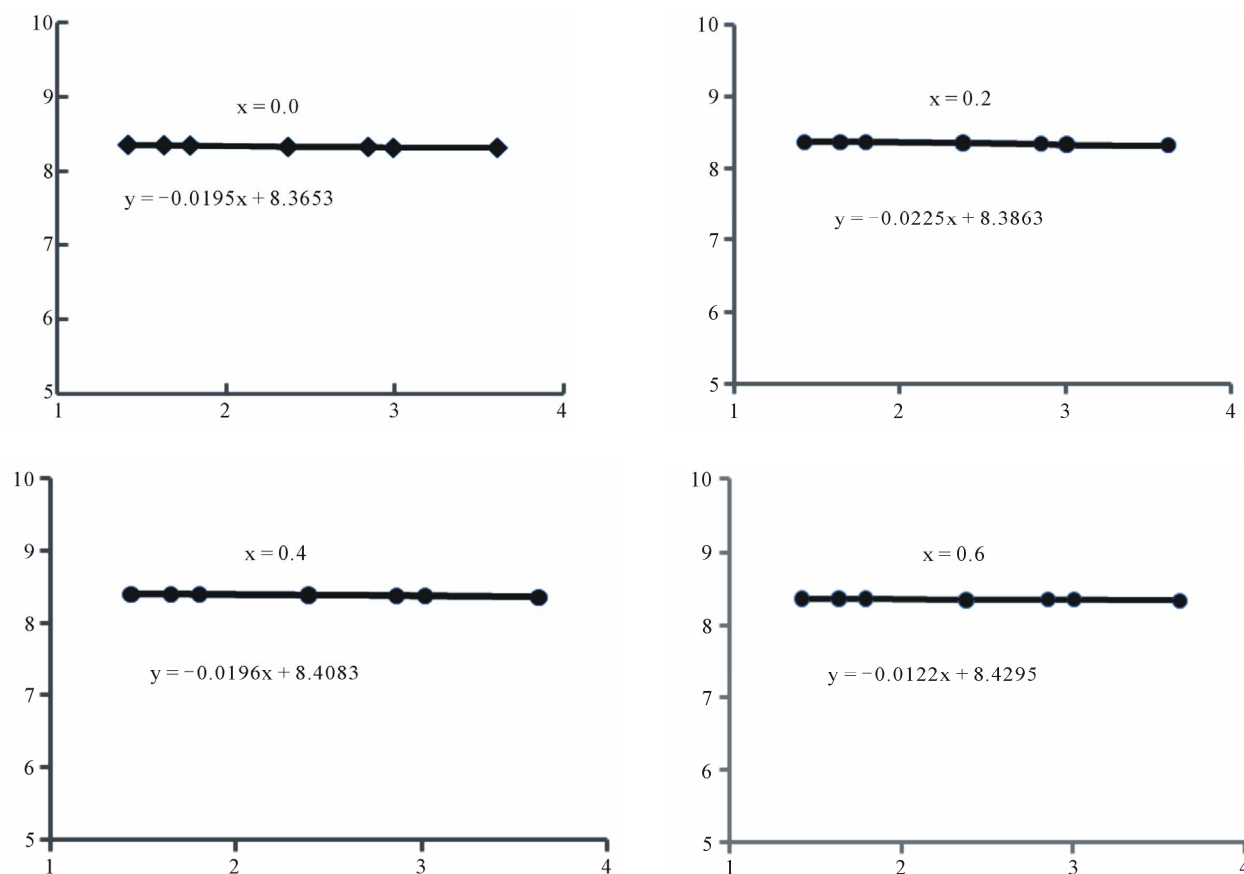


Figure 2. Variation of lattice parameter with N-R function.

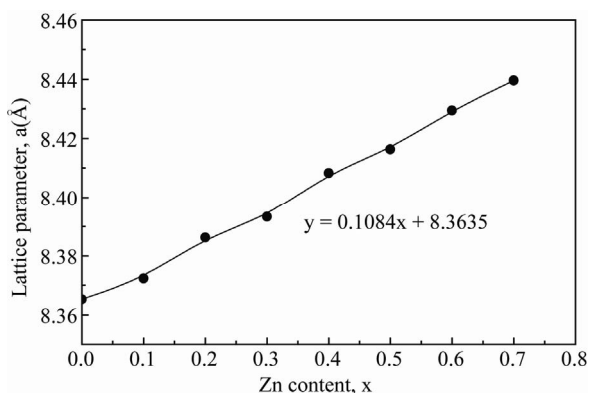


Figure 3. Variation "a" with Zn content.

radius of Zn^{2+} ions ($R_{\text{Zn}^{2+}} = 0.82 \text{ \AA}$) [11] is larger than that of Cu^{2+} ions ($R_{\text{Cu}^{2+}} = 0.73 \text{ \AA}$) [12], the substitution is expected to increase the lattice constant with the increase in x throughout the concentration studied. A similar linear variation has also been observed in Zn-Mg [8], Li-Mg [13]; Zn-Mg-Cu [14]; Zn-Mg [15]; and Li-Cd [16] ferrites. It was reported [17] that the value of lattice constant of CuFe_2O_4 is 8.380 \AA . Our experimental value is 8.365 \AA , which is almost similar to the reported value. This slight

difference in the value of the lattice constant is may be due to the different scattering source, different sintering and preparation techniques.

The bulk density, ρ_B , was measured by usual mass and dimensional consideration whereas X-ray density, ρ_x , was calculated for each sample using the expression [18]

$$\rho_x = \frac{ZM}{Na^3}$$

where, M is the molecular weight of the corresponding composition, N is Avogadro's number, $V = a^3$ is the volume of the cubic unit cell and Z is the number of molecules per unit cell, which is 8 for the spinel cubic structure. The porosity percentage was then calculated from ρ_B and ρ_x values using the expression [19]

$$P = \left(1 - \frac{\rho_B}{\rho_x}\right) 100$$

Density plays a key role in controlling the properties of polycrystalline ferrites [20,21]. The variation of X-ray and bulk densities is shown in **Figure 4**. By substituting Zn in Cu-Zn ferrite, a decrease of X-ray and bulk densities is observed. The X-ray density depends upon the

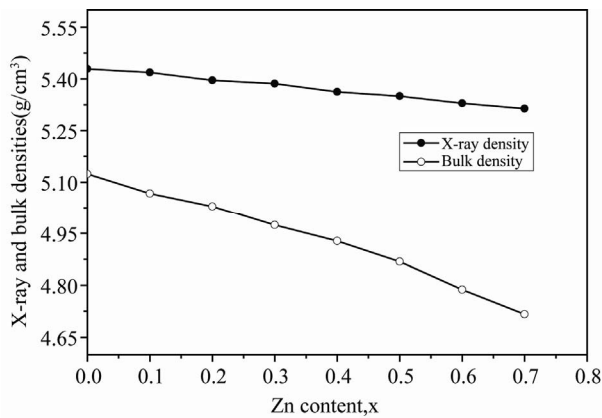


Figure 4. X-ray and bulk densities with Zn content.

lattice constants and molecular weight of the samples. As lattice constants increase linearly with the increase of Zn content, X-ray density decrease owing to the stoichiometry of the sample. Similar decrease pattern is observed by A. A. Pandit *et al.* in Mg-Mn ferrite [22]. It is also observed from Figure 4 that the X-ray densities are larger in magnitude than corresponding to bulk densities. This may be due to the existence of pores which were formed and developed during the sample preparation or the sintering process [23].

The effect of Zn ion on bulk density and on the porosity is shown in Table 1 and Figure 5. By incorporating Zn into Cu-Zn ferrite, a significant decrease of the bulk density can be obtained. The highest density 5.124 g/cm³ whereas lowest porosity 5.61% is obtained for the composition of $x = 0.0$ *i.e.* for pure Cu-ferrite. The porosity value of all the samples is less than 12% that indicates the existence of very few pores in the samples. The porosity is found to increase from 5.61% for $x = 0.0$ to 10.18% for $x = 0.7$. Moreover this increase in porosity and decrease in bulk density is due to the increase in grain size, because the grains may be of irregular shape and as the sintering proceeds the grain growth takes place [24]. The intergranular pores as developed during sintering must also be capable of moving with the grain boundaries as the growth occurs, requires that the pores move together and coalesce, and a different transport mechanism has been indicated. This consists of the transport of gaseous oxygen across the pores and the diffusion of cations around the pores; it is facilitated by high concentration of cation vacancies *i.e.* excess of Fe_2O_4 . Hence it is concluded that porosity increase with the addition of Zn content due to the creation of more cation vacancies with the reduction of oxygen vacancies [25].

Structural and magnetic properties sensitively depend on the microstructure of ferrites. Grain size of the microstructures is the most important parameter affecting the magnetic properties of ferrites. Figure 6 shows the SEM

Table 1. Lattice Constant, Bulk density, X-ray density and porosity of the system $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$.

Mn content (x)	Lattice Constant, a_0 (Å)	Bulk Density, ρ_B (gm/cm ³)	X-ray Density, ρ_x (gm/cm ³)	Porosity (%)	Grain size (µm)
0.0	8.3653	5.124	5.43	5.61	3.822
0.1	8.3724	5.067	5.42	6.49	3.577
0.2	8.3863	5.029	5.40	6.79	3.325
0.3	8.3934	4.974	5.39	7.65	2.902
0.4	8.4083	4.928	5.36	8.09	2.396
0.5	8.4164	4.868	5.35	9.02	2.047
0.6	8.4295	4.787	5.33	10.18	1.565
0.7	8.4396	4.716	5.31	11.26	1.277

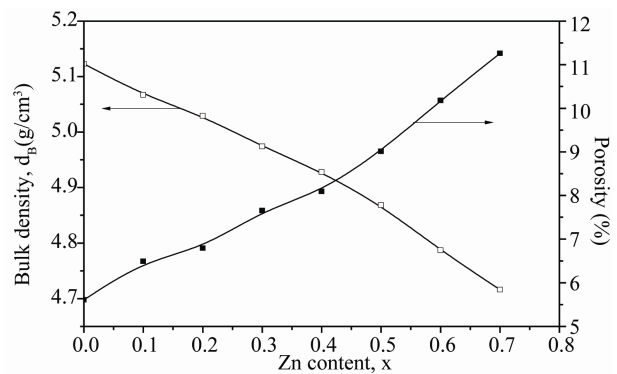


Figure 5. Bulk density and Porosity with Zn content.

photographs of Cu-Zn ferrites substitute with Zn content of 0.0, 0.2, 0.4 and 0.6 respectively. The average grain size was obtained by line intercept method using SEM. As shown in Figure 6, the microstructures revealed that the grain size was influenced by the Zn substitution. From Table 1, it is observed that with the increase of Zn substitution, the grain size decreased. In general, the grain sizes of all samples are smaller than 4 µm, which is superior to reduce thickness of each layer in multilayer chip inductors leading to further miniaturization.

The structural and magnetic properties of soft ferrites are influenced by the composition, additives and microstructures of the materials. Among these factors, the microstructures have great effect on structural and magnetic properties. It is generally known that the larger grain sizes, the higher the saturation magnetization and initial permeability. Figure 7 shows permeability increased with the increase of Zn content upto $x = 0.5$ and after that it decrease. However, the variation of initial permeability with Zn content was not consistent with the variation of microstructures, the bulk density and the above empirical

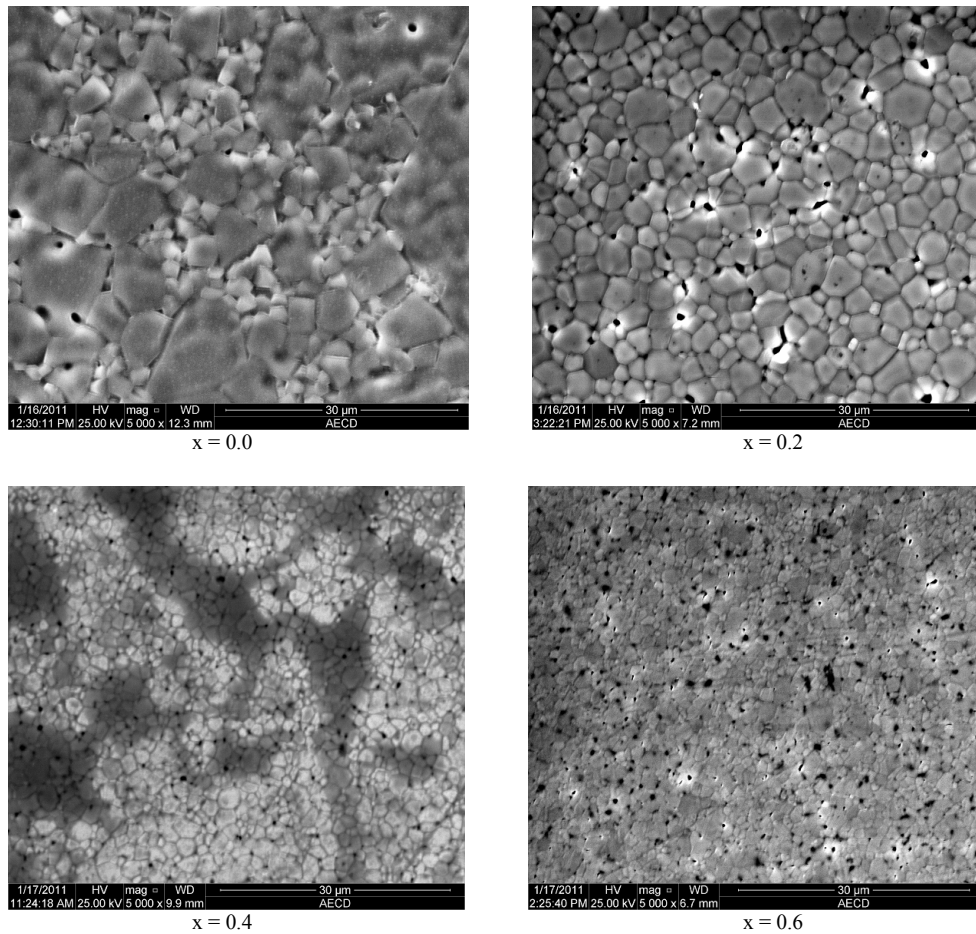


Figure 6. SEM micrographs of $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrites ($x = 0.0, 0.2, 0.4, 0.6$).

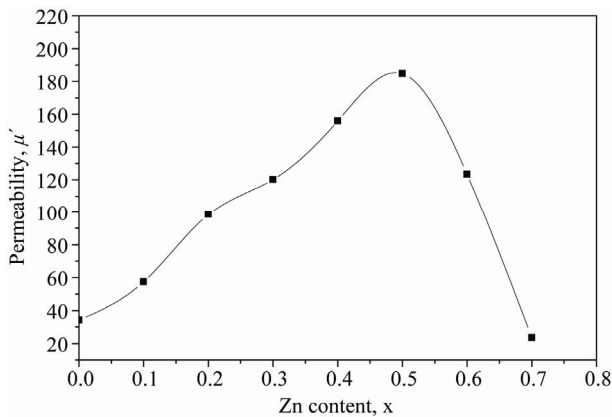


Figure 7. Variation of initial permeability at with Zn content 10 KHz.

principle. This phenomenon might be explained by the following equation:

$$\mu_i \propto M_s^2 / (aK + b\lambda\sigma)$$

where μ_i is the initial permeability, M_s is the saturation

magnetization, K is the crystal anisotropy constant, λ is the magnetostriction constant, and σ is the inner stress. Nam *et al.* studies [26] that Zn substitution within small range in composition plays a crucial role in properties of NiCuZn ferrites by reducing magnetostriction effects. Therefore with the increase of Zn content, the increase of the initial permeability of CuZn ferrites was attributed to the decrease of magnetostriction constant. The same conclusions have been confirmed by Nakano's [27] and Xiwei qi's [28] studies. From microstructures we could see that the grain sizes tended to become smaller and the distributions of pores were more even which might help to diminish inner stress and lead to an increase of initial permeability. In comparison with the reported results of NiCuZn ferrites prepared by the same method [26], low temperature sintered CuZn ferrites possess higher initial permeability and better grain structure. The higher initial permeability, low cost, low sintering temperature and smaller grain size characteristics make the Zn substituted CuZn ferrites be the most potential candidate material for Multilayer chip inductor (MLCI) industry.

4. Conclusions

A series of $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrites have been synthesized. The presence of Zn ions causes appreciable changes in the structure and physical properties of the Zn-substituted Cu-Zn ferrite. XRD results indicate the single phase of pure cubic spinel structure. The lattice constant is found to increase linearly with increasing Zn content in the mixed Cu-Zn ferrite system obeying Vegard's law due to larger ionic radius of Zn^{2+} compared to Cu^{2+} . X-ray density decrease with increasing Zn content as lattice constant increase. A remarkable decrease in the value of bulk density has been found with increasing Zn substitution Cu-Zn ferrite attaining 98% of theoretical density for the sample $x = 0.0$. The porosity is found to increase for the Zn substitution due to the creation of more cation vacancies with the reduction of oxygen vacancies. With the increase of Zn substitution, the grain sizes decreased. The increases of initial permeability of CuZn ferrites with Zn content were attributed to the decrease of magnetostriction constant.

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