Effect of Mg substitution on electromagnetic properties of $(Ni_{0.25}Cu_{0.20}Zn_{0.55})Fe_2O_4$ Ferrite prepared by auto combustion method

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Abstract

The ferrite compositions of $(Ni_{0.25-x}Mg_xCu_{0.2}Zn_{0.55})Fe_2O_4$ with x =0.0, 0.07, 0.13, 0.18, and 0.25 were synthesized through nitrate-citrate auto-combustion method. The as-burnt powders showed the presence of crystalline cubic spinel ferrite with about 19-22 nm crystallite sizes. The resultant powders were calcined at 700°C/2h and pressed ferrites were sintered at 950°C/4h. The initial permeability, magnetic loss and AC resistivity were measured in the frequency range 10Hz to 10MHz. The permeability and AC resistivity were found to increase and the magnetic loss decreased with Mg substitution for Ni, up to x=0.18. The very high permeability in the composition x=0.18, was due to better densification, lower magnetostriction constant and inner stresses etc. The AC resistivity of the composition was also highest. The composition would be better than NiCuZn based material for more miniaturization of multi layer chip inductor.

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Keywords: Soft ferrite; Mg substitution; NiCuZn ferrites; electromagnetic properties; magnetostriction constant

1. Introduction

With the rapid development of mobile communication and information technology, the electronic component with small size, high efficiency, and low cost are urgently demanded [1]. Multilayer Chip Inductor (MLCI) is such a component, widely

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used in electronic products, such as cellular phone, notebook computer, and video cameras [2]. Up to now, Ni-Cu-Zn ferrites have been the dominant materials for MLCI due to its better magnetic properties at high frequency and low sintering temperature [3-4]. Mg-Cu-Zn ferrite is also a pertinent magnetic material for wide applications owing to its high resistivity, high Curie temperature, and environmental stability [5]. Materials with high permeability are required for reducing the number of layers in MLCI and realizing the better miniaturization [5]. It is believed that initial permeability can be increased by decreasing magnetostriction constant also [6]. As the magnetostriction constant of Mg-Cu-Zn ferrite is lower than that of Ni-Cu-Zn ferrite, MLCI using Mg-Cu-Zn ferrite would obtain higher magnetic properties [6]. Mg-containing composition is also preferred to avoid the presence of divalent iron (to obtain high resistivity) and to avoid the tendency of discontinuous grain growth (an essential requirement to obtain a dense ferrite) [7]. It is then expected that Mg addition in Ni-Cu-Zn ferrite may improve the electromagnetic properties. With this idea, the effects of Mg substitution for Ni on the electro-magnetic properties of $(Ni_{0.25}Cu_{0.2}Zn_{0.55})Fe_2O_4$ ferrite has been investigated in the present work. So far the knowledge of authors no literatures are available on this aspect. The ferrite powders are synthesized through nitrate-citrate auto combustion route to get nano sized particles with good sinterability.

2. Experimental

Analytical grade Magnesium Nitrate [$Mg(NO_3)_2.6H_2O$], Zinc Nitrate [$Zn(NO_3)_2.\ 6H_2O$], Copper Nitrate [$Cu(NO_3)_2.3H_2O$], Iron Nitrate [$Fe(NO_3)_2.\ 9H_2O$] and Citric Acid [$C_6H_8O_7.H_2O$] were used to prepare $(Ni_{0.25-x}Mg_xCu_{0.20}Zn_{0.55})\ Fe_2O_4$ with x =0.0, 0.07, 0.13, 0.18, and 0.25 by sol-gel auto-combustion method. Metal nitrates and citric acid were dissolved in deionized water and were mixed in 1:1 molar ratio of nitrates to citric acid. The pH of the solution was adjusted to 7 using ammonia solution. Then the solution was heated at 80ºC to transform into gel. When ignited at any point of the gel, the dried gel burnt in a self-propagating combustion manner until all gels were completely burnt out to form a fluffy loose powder. The as-burnt precursor powder was then calcined at 700ºC for 2hr. The calcined ferrite powder was granulated using PVA as a binder and were uniaxially pressed at a pressure of 2 ton/cm^2 to form toroidal and pallet specimens.

The specimens were sintered at 950^0C for 4hr in air atmosphere. The as-burnt ash, calcined powders and the sintered ferrites were characterized with respect to phase identification, crystallite size and lattice parameter determination using X-ray diffraction (PW-1830, Philips, Netherlands) with CuKα radiation. The bulk density and porosity of sintered ferrites were measured using the Archimedes principle. The impendence analyzer (Hewlett Packard, Model 4192A, USA) was used to measure the inductance and the magnetic loss factor on toroids, wound with low capacitive 6 turns enameled copper wire. The resistivity was measured on pallet samples by applying silver electrodes on the surfaces.

3. Results & Discussion:

The XRD patterns in Fig.1 shows that the as-burnt ferrite powders are in crystalline state and contain cubic spinel ferrite phases similar to JCPDS card No. 08-0234. No second phase was detected by XRD. This reveals that the Mg substituted Ni-Cu-Zn ferrite powders can be synthesized directly from the auto-combustion of citrate-nitrate gels. The broad peaks in XRD patterns indicate fine crystallite size of the ferrite particles. The crystallite size was calculated from XRD peak broadening of the [311] peak using Scherrer formula. The crystallite size of ferrites were in the range 19-22nm for as burnt powder and 32-34nm when burnt ashes were calcined at $700^oC/2h$. No noticeable influence of Mg on the crystallite size formation was observed.

The sintered ferrites were also characterized by XRD. The crystallite size and lattice parameter of sintered ferrites are shown in Table 1 along with their bulk density, percent theoretical density, percent closed porosity, permeability and resistivity. The theoretical density is the X-ray density (d_x), calculated according to relation; $d_x = ZM/Na^3$, where Z is the number of molecules per unit cell (Z=8), M is the molecular weight, N is Avogadro's number and a^3 is the volume of unit cell. The bulk density increases with Mg-addition upto x=0.18 composition. The lower bulk density of Mg-Cu-Zn ferrite i.e. x=0.25 composition may be due to the absence of Ni in the composition. This reveals that the Mg addition reduces liquid formation temperature in Ni-Cu-Zn ferrite. The composition x=0.18 has highest density and lowest porosity, although, the major part of that porosity is closed porosity. It is difficult to remove closed porosity completely due to the evaporation of constituents specially Zn. The amount of closed porosity increases with Mg (x) content due to the formation of higher amount of liquid phase and hence higher rate of densification. The crystallite size in sintered body also shows that the compositions with x=0.0 & x=0.25, have lower size (grain growth) may be due to the lower amount of liquid phase formation compared with compositions containing both Ni & Mg. No noticeable change is found in lattice parameter of the ferrite in different compositions as radius of $Mg^{+2} \approx Ni^{+2}$.

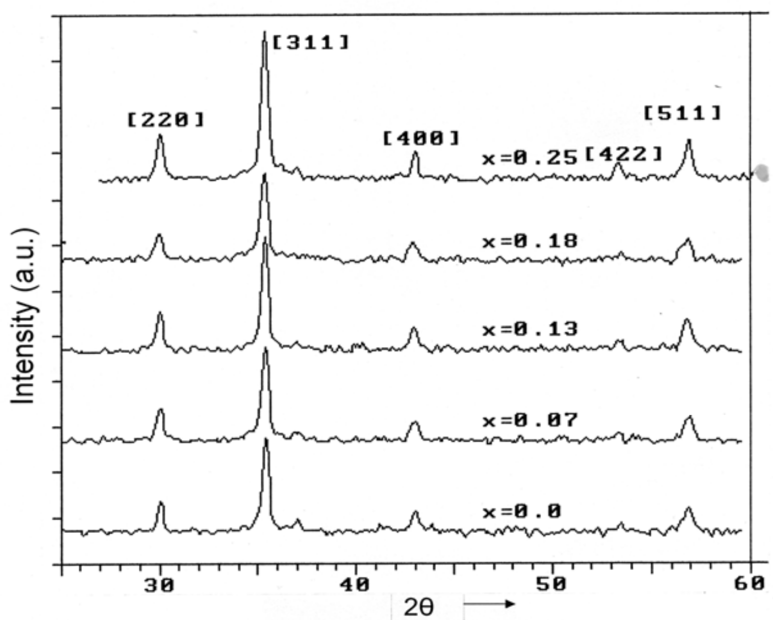

Fig.1 XRD patterns of as burnt ($Ni_{0.25-x}Mg_xCu_{0.20}Zn_{0.55}$) Fe_2O_4 ferrites with different Mg (x) content.

As shown in the Fig. 2 (also in Table 1), permeability increases with the increase in Mg (x) content in Ni-Cu-Zn ferrite. It may be noted that the permeability values are corrected with respect to porosity contributions as per [8]. The increase in initial permeability with Mg content may be primarily attributed to the increase in bulk density. It is known that ferrites with higher density and larger average grain size possess a higher initial permeability [9]. An increase in the density, not only results in the reduction of demagnetizing field due to the presence of pores but also raises the spin rotational contribution, which in turn increase the permeability [10]. It is interesting to note a sharp increase in permeability of the composition with x = 0.18. That sharp increase can not be fully explained considering density and grain size parameters. In fact, the initial permeability of ferrite is usually expressed as follows; $\mu = M_s^2 / (aK+b\lambda\sigma)$, where μ is the initial permeability, M_s the saturation magnetization, K the crystal magnetic anisotropy, λ the magnetostriction constant, σ the inner stress, a and b are constants. So, the major part of the increased permeability in x=0.18 composition is attributed to the decrease in magnetostriction constant mainly and may be in parts, decrease in the anisotropy and inner stresses in this narrow composition range. However, the initial permeability of the composition x=0.25 is much lower than the composition x=0.18. This may be attributed to the lower bulk density, lower crystallite size and absence of Ni in the composition.

Table 1

Bulk density, percent theoretical density, percent closed porosity, crystallite size, lattice parameter, permeability (porosity corrected) and resistivity for sintered $(Ni_{0.25-x}Mg_xCu_{0.20}Zn_{0.55}) Fe_2O_4$ ferrites with different Mg (x) content.

"x" (Mg-Content)	Bulk Density (gm/cc)	Theoretical Density (%)	Closed porosity (%)	Crystallite Size (nm)	Lattice parameter (Å)	Permeability (μ)	Resistivity (ohm-cm) at 100kHz
0	3.47	65.1	2.15	65.4	8.4129	268	1.2×10^6
0.07	4.34	81.9	4.81	124.7	8.3991	680	5.4×10^6
0.13	4.44	84.4	5.69	121.9	8.3991	940	6.3×10^6
0.18	4.70	90.5	7.46	127.6	8.4097	2420	4.2×10^7
0.25	4.26	82.7	5.64	84.7	8.4083	502	2.6×10^6

Fig. 3 shows the Frequency dependency of the permeability in $(Ni_{0.25-x}Mg_xCu_{0.2}Zn_{0.55}) Fe_2O_4$ ferrites with different Mg (x) content. The permeability is stable in the frequency range 100 kHz to 2MHz and its dispersion occurs about above 2MHz frequency. It is known that the high frequency dispersions are associated with domain wall dynamics [11]. The increase in frequency dispersions with Mg content indicates the critical field decreases due to the Mg incorporation. This decrease in cut-off frequency with increase in Mg(x) content is attributed to the increase in initial permeability following Snoek's law.

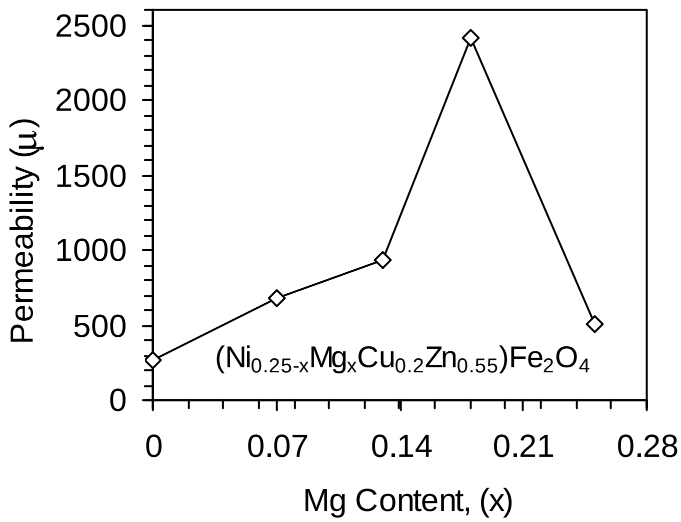

Fig.2 Permeability as a function of Mg (x) content in $(Ni_{0.25-x}Mg_xCu_{0.20}Zn_{0.55})$ Fe_2O_4 ferrites.

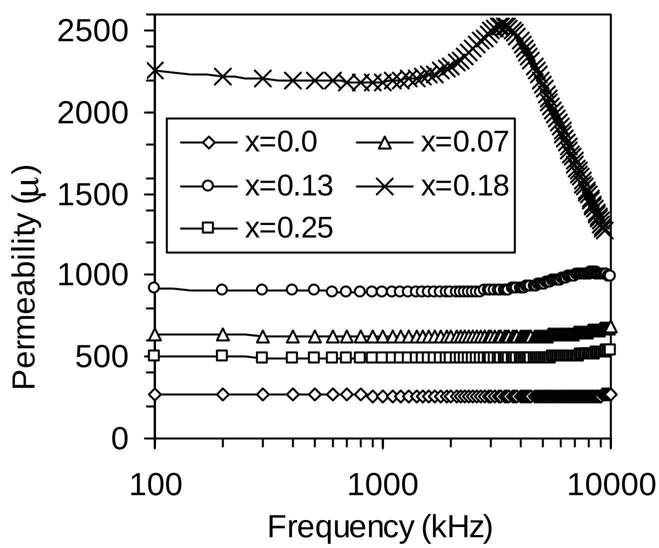

Fig. 3 Frequency dependency of permeability in $(Ni_{0.25-x}Mg_xCu_{0.2}Zn_{0.55})Fe_2O_4$ ferrites with different Mg (x) content.

Fig. 4 shows the relative loss factor (RLF) i.e. the ratio of the magnetic loss tangent to the initial permeability. A high μ and low tanδ i.e. the low RLF is required for high frequency magnetic applications. The figure shows that the RLF decreases with Mg-substitution. The RLF of composition x=0.0, is slightly higher in lower frequency range (kHz), may be due to mainly higher hysteresis losses arising from its porous (porosity ~ 35%) structure. It is known that hysteresis losses increase with the increase in porosity [12]. The RLF of all the cores increase in MHz frequency zone due to the resonance-relaxation losses. The composition with x=0.18 has lowest RLF and hence is the best material upto ≈ 2 MHz frequency applications.

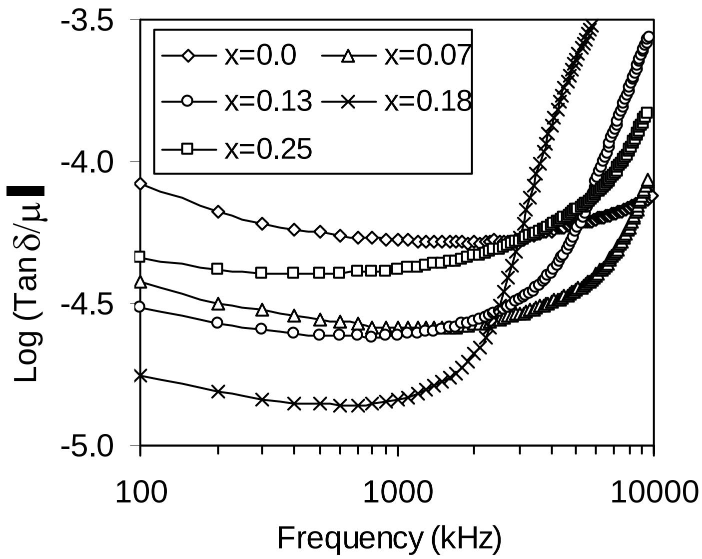

Fig. 4 Relative loss factor as a function of frequency in $(Ni_{0.25-x}Mg_xCu_{0.2}Zn_{0.55})Fe_2O_4$ ferrites with different Mg (x) content.

The electrical resistivity is an important property of low temperature sintered ferrite for MLCI application. Fig. 5 shows the frequency dependency of AC resistivity for different compositions. The resistivity of Ni-Cu-Zn ferrite increases with the increase in Mg content upto x=0.18 (Table 1) and on an average the resistivity of all the compositions decrease with the increase in frequency (Fig.5). The conduction mechanism in ferrite is considered as the electron hopping between Fe^{2+} and Fe^{3+} in B site. The lowest resistivity of composition x=0.0, may be attributed to the presence of higher amount of Fe^{2+} ions in the ceramics. It is known that the formation of Fe^{2+} may be expected owing to the partial reduction of Fe^{3+} to Fe^{2+} and evaporation of Zn ions during the sintering process [13]. The re-oxidation of Fe^{2+} and the formation of Ni^{3+} are also expected during cooling of ferrites after sintering, due to absorption of oxygen [14]. So the increase in resistivity with Mg-addition may due to the decrease in Fe^{2+} [7] and Ni^{3+} ionic concentrations.

However, it is interesting that the highest Mg containing composition (x=0.25) has lower resistivity than x=0.18 composition. This observation is yet to be explained properly. The probable reasons may be the absence of Ni in the composition x=0.25 and the formation of highly resistive grain boundary phase in the composition x=0.18.

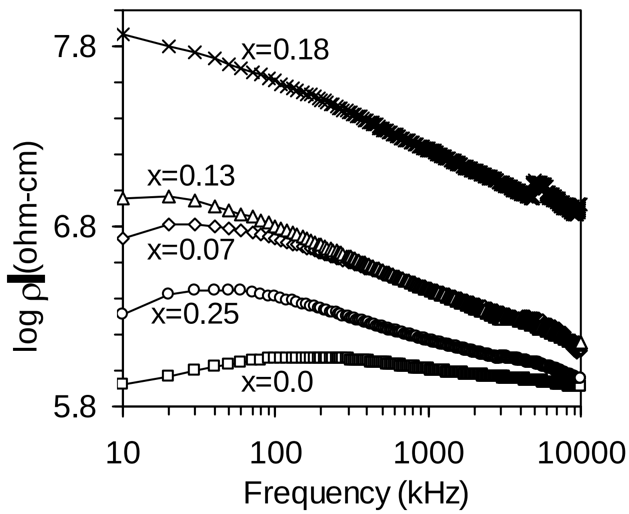

Fig. 5 AC Resistivity as a function of frequency in $(Ni_{0.25-x}Mg_xCu_{0.2}Zn_{0.55})Fe_2O_4$ ferrites with different Mg (x) content.

4. Conclusions

The Effects of Mg substitution for Ni in NiCuZn ferrite was investigated and reported first time. An improved electromagnetic property of the Mg substituted ferrite was found. The highest permittivity, lowest relative loss factor and highest AC resistivity was found in the composition $(Ni_{0.07}Mg_{0.18}Cu_{0.2}Zn_{0.55})Fe_2O_4$. The better electromagnetic properties were due to the better densification, lower magnetostriction constant and higher resistivity of the said composition. This composition would be a better material than Ni-Cu-Zn based composition for reducing the number of layers in MLCI and realizing more miniaturization.

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