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Investigation the effect of Cu^{2+} substitution on the electro-magnetic properties of NiZn ferrite nanostructures

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Abstract

NiCuZn ferrite is widely used for the manufacturing of multilayer chip inductors (MLCIs) due to its good electromagnetic properties and low sintering temperature (<950°C). In this study, the $Ni_{0.50-x}Cu_xZn_{0.5}Fe_2O_4$ nanopowders with different Cu contents (x=0.15, 0.20 and 0.25) were prepared through the nitrate citrate combustion method. The prepared nanopowders were calcined at 600 °C, compacted and sintered at 900 °C. The micristructural and electromagnetic properties were investigated as a function of Cu content. XRD analysis showed the formation of cubic spinel phase for all samples. A significant increase in density from 4.66 to 4.82 g/cm^3 were observed with increasing Cu content. The microstructural evaluations revealed that Cu can affect the densification and porosity of the samples. The electromagnetic results revealed that the magnetic permeability increased with Cu content and the highest value of 161 was obtained at x = 0.25.

1. Introduction

Recently, with the rapid development of miniaturization trend of electronic devices, spinel ferrite has been applied of intensive research. The spinel ferrites become important from both the fundamental and application point of view as they got potential use in multi-layer chip inductors (MLCIs) and LC filters. NiZn ferrite has been extensively studied to MLCIs due to their excellent magnetic properties like, high electrical resistivity, high permeability in the radio frequency range, and environmental stability [1-3].

It is well-known that introduce ions into Ni based ferrites can improve their electrical and magnetic properties. For example, manganese ions (Mn^{2+}) increase the resistivity of ferrite due to the change in the valence state, and calcium ions (Ca^{2+}) segregate at the grain boundaries to form a secondary phase. Magnesium ions (Mg^{2+}) tend to occupy tetrahedral sites with a corresponding migration of Fe^{3+} ions from tetrahedral to octahedral sites and as a results increase the saturation magnetization. The copper ions (Cu^{2+}) reduce the sintering temperature and improve the density of nickel ferrites [4-6].

On the other hand, the magnetic propertiy of a ferrite is strongly dependent on method of preparation and chemical composition. Moreover, the applications of magnetic nanostructures require narrow particle size distribution and a specific particle size. Thus, preparation of nanostructured ferrite could improve densification and sintering activity. Bbecause nanoscale powders have the potential to tailor shrinkage versus temperature behavior. Ferrites nanopowders are prepared through various methods like, sol-gel, high energy ball milling, microwave sintering chemical co-precipitation, and combustion methods [7-10]. The combustion method is a unique method for the synthesis of nanostructure ferrites with high sintering activity to dense at less than 900 °C [11]. The aim of this work is to study the effect of Cu^{2+} ions on the structure, microstructure and electromagnetic properties of nanocrystalline of $Ni_{0.50-x}Cu_xZn_{0.5}Fe_2O_4$ powder ferrites.

2. Preparation of samples

The NiCuZn ferrite powders were prepared by analytical grade of nickle nitraie, zinc nitrate, cooper nitrate, iron nitrate and citric acid through the auto combustion technique. The Ni-nitrate, Zn-nitrate, and Cu-nitrate were dissolved in water. Then, the solution of citric acid was mixed to the previous solution in 1:1 M ratio of metal nitrates to citric acid. Ammonia was added to adjust pH value to 7. The resultant under constant stirring was heated to form into a xero-gel. After that, the prepared gel burnt out to form a fluffy powder. The prepared powder for 2 hours was calcined at 700 ºC, and uniaxially pressed into toroid shape. The prepared toroids were sintered for 4 h at 900 ºC. The structural and magnetic properties of prepared samples were studied by XRD, SEM, VSM and RF-Impedance analyzer (Agilent 4991A).

3. Results and discussion

The XRD patterns of the prepared nanopower (x=0.15) and sintered samples are shown in Fig. 1. The as-burnt nanopowder shows the main peaks corresponding to typical NiCuZn ferrite spinel structure with high crystallization. The crystallite size of the ferrite nanopowder was calculated to 23 nm using Scherer's equation. The sintered ferrites present the intense peaks that indexed as a single phase cubic spinel structure (JCPDS No. 08-0234). It can be seen, there are no any other impurity phases in the patterns. Table 1 shows the crystallite size of the samples increases with Cu content and are in the range 59–70 nm. The lattice parameters ‘a’ was determined using the relation $1/d^2=(h^2+k^2+l^2)/a^2$ where d is the inter-planar distance and (hkl) are the Miller indices. Results show the values of ‘a’ do not show significant variation with increasing Cu substitution for Ni. This is attributed to the same ionic radius of Cu^{2+} (0.73 Å) and Ni^{2+} (0.74 Å).

Fig. 2 illustrates the variation of bulk density of the prepared samples. It is seen that the density increases with the Cu content. The effect of Cu^{2+} ions on the densification of sinterd samples can be explained by the sintering mechanism based on mobility of ions at relatively low temperatures. According to the solid solution formation mechanism the higher mobility of Cu^{2+} ions increases the permeation path, thereby increasing the rate of internal permeation in the solid solution.

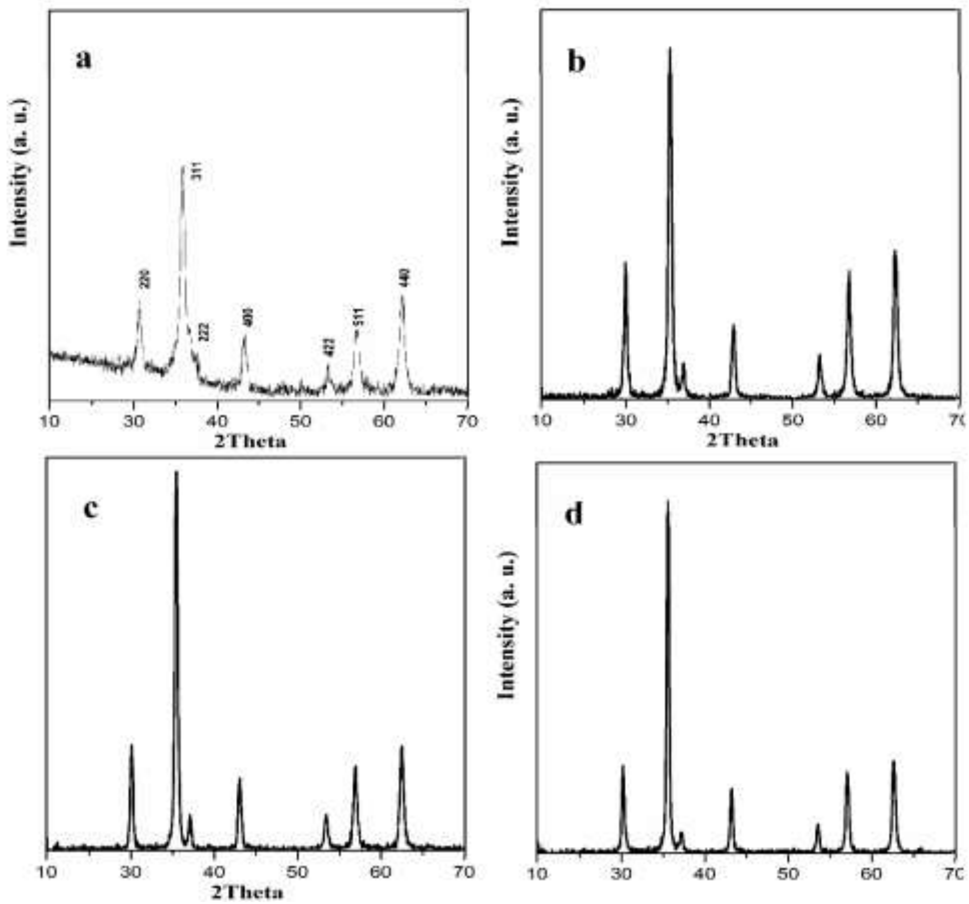

Fig. 1. XRD patterns of $NiCuZnFe_2O_4$ (a) nanopowder and sinterd samples with x= (b) 0.15 (c) 0.20 and (d) 0.25.

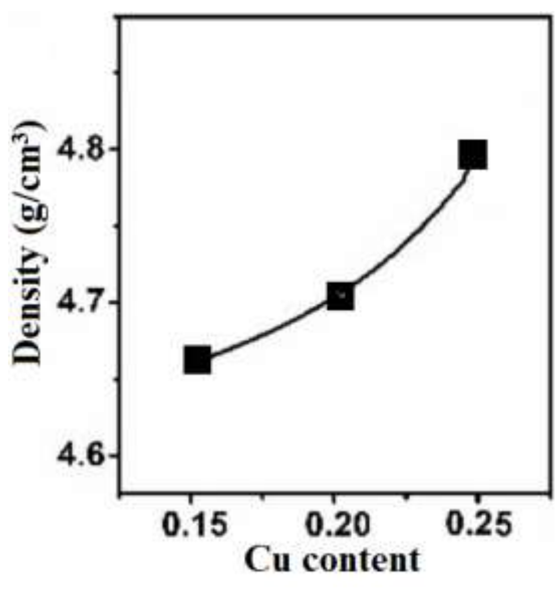

Fig. 2. Variation of bulk density of sinterd samples with Cu content.

The SEM photographs of the $Ni_{0.50-x}Cu_xZn_{0.5}Fe_2O_4$ naonopowder (x=0.15) and sintered samples (x=0.15, 0.20 and 0.25) are depicted in Fig. 3. The SEM micrograph of nanopowder shows that NiCuZn ferrite nanopowders are spherical in shape with a very small size of less than 50 nm (Fig. 3a). As shown in Fig. 3b-d, the morphology of samples reveal that the grain size is influenced by the Cu. With the increase of Cu^{2+} concentration from 0.15 to 0.25 the porosity decreases. The micrograph of the sample with x=0.15 shows the existence of many pores distributed at the grain boundaries. Such porous structure can explain why the its bulk density is lower than other samples. According to Lange and Kellet [12] grain growth, pores and densification are intimately related. The sample with x= 0.25 and higher density has morphology with lower porosities.

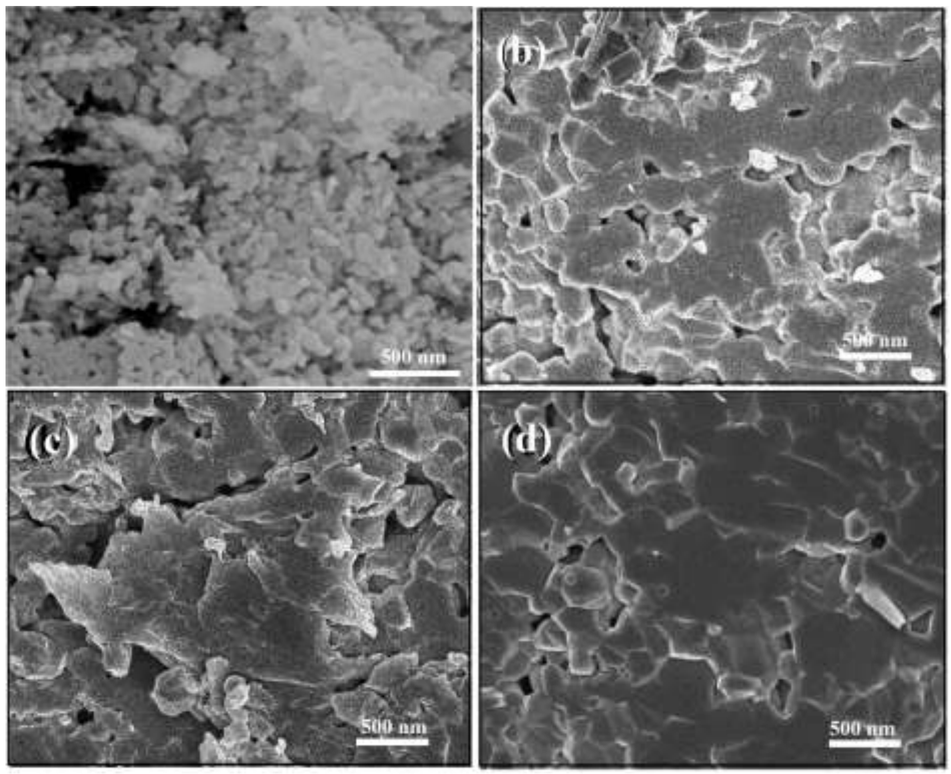

Fig. 3. SEM images of $NiCuZnFe_2O_4$ (a) nanopowder and sinterd samples with x= (b) 0.15 (c) 0.20 and (d) 0.25.

It is well known that in the ferrites, permeability are influenced by the intrinsic factors (preferential site occupancy) as well as the extrinsic factors (grain size and porosity) [7].

Fig. 4 shows the permeability (μ_i) of sintered samples as a function of frequency with various content of Cu. It is seen that the value of μ_i for each sample remains constant in the frequency range up to a critical frequency, which is called the resonance frequency.

The permeability of the samples was found to increase with the increase in Cu content from 103 to 161 but, f_r moves towards the lower frequency. This observation is in agreement with the snoek's law which says the initial permeability and resonance frequency are related inversely. It has been showed that ferrite materials with uniform grain size, high density, and high phase purity is beneficial to have high μ_i values [13]. As demonstrated above, the increase in Cu^{2+}

ions can improve the density and grain size of the sinterd samples, which increases the μ_i value. However, the Cu^{2+} ions show 1.3 μ_B, which is smaller than the 2.3 μ_B of nickel ions (Ni^{2+}). Replacing Ni^{2+} at the octahedral sites with Cu^{2+} results in a decrease in saturaton magnetization. Thus, the increasing μ_i with Cu^{2+} content results from the combined effects of cation distribution and microstructure.

Table 1. Crystallite size, Lattice parameter (a), Bulk density (ρ_b), and initial permeability (μ_i) of sintered NiCuZn ferrite.

x	Crys. Size (nm)	a (Å)	ρ_b [g/cm^3]	μ_i (1 MHz)
0.15	59	8.61	4.66	103
0.20	61	8.60	4.71	142
0.25	70	8.62	4.82	161

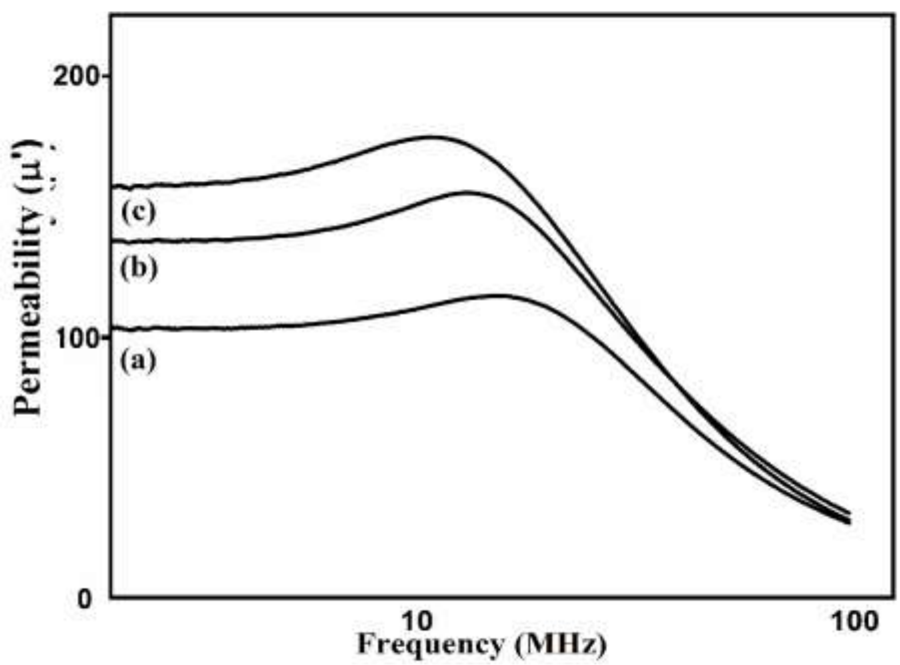

Fig 4. Permeability of the sinterd toroid with x= (a), 0.15 (b) 0.20 and (c) 0.25.

4. Conclusion

$Ni_{0.50-x}Cu_xZn_{0.5}Fe_2O_4$ (x=0.15, 0.20, 0.25) nanopowders synthesized by the nitrate-citrate combustion method, showed high sintering activity. The XRD results showed the formation of cubic spinel structure. The bulk density is found to increase with Cu content. The morphology evaluations revealed that the densification and grain growth are influenced and increased by Cu^{2+} substitution. The electromagnetic results revealed that the initial permeability increases with Cu^{2+} content and the highest value of 161 was obtained at x = 0.25.

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