

Complex permittivity and permeability of Co-substituted NiCuZn ferrite at rf and microwave frequencies

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Abstract NiCuZn ferrite has recently attracted a lot of attention for its application in high frequency (up to a few GHz) multilayer chip inductors (MLCIs) and for other microwave devices owing to their favorable electromagnetic properties and low densification temperature. In order to study the effect of substitution of cations by cobalt in small concentration on the dielectric and magnetic properties at low and high frequencies, bulk polycrystalline ferrite samples of starting composition $(\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6})_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$, having $x = 0, 0.01, 0.03$ and 0.05 , were prepared by citrate precursor method. Pure spinel (cubic) ferrite formation was confirmed by powder X-ray diffraction technique. Complex permittivity and permeability were measured at microwave frequencies (X-band) using the cavity perturbation method, which is a non-contact method. The values of real part of permittivity (ϵ') vary in the range 7–9.6 and of the imaginary part (ϵ'') vary from 0.020–0.120, whereas real part of the permeability (μ') lies in the range 2.6–14.0 and the imaginary part of permeability (μ'') varies from 0.5–6.0. It is observed that there is an increase in μ' and decrease in the magnetic loss ($\tan \delta_\mu$) on increasing the cobalt concentration from $x = 0$ to $x = 0.05$. The variation of these parameters, both with frequency in X-band and with the cobalt concentration, is discussed in this paper.

Keywords NiCuZn ferrite · Citrate precursor method · Complex permittivity and permeability

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Introduction

Ni-Zn ferrite is widely used in many applications, including multilayer chip inductors (MLCIs), microwave components and devices [1–4]. Substitution of copper in these ferrites is known to improve the sintering properties drastically [5]. For the application of these ferrites in high frequency devices, the material should have low losses at high frequencies. Addition of small amounts of Co is reported [6, 7] to reduce the magnetic losses and anisotropy. Performance characteristics of the ferrites prepared by the chemical methods have exhibited improvement over to ferrites prepared by the conventional solid state sintering method [4, 8, 9].

In the present paper, polycrystalline $(\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6})_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ferrite samples were synthesized by non-conventional chemical citrate route. The effect of addition of small amount of Co on dielectric and magnetic properties of Ni-Cu-Zn ferrite as well as on the losses at rf and microwave frequencies is studied.

Experimental

$(\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6})_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.01, 0.03$ and 0.05) powders were synthesized by the citrate precursor method using metal nitrates and citrates of analytical grade purity. The starting materials were iron (III) citrate (Merck, Germany), nickel nitrate (Merck, India), copper nitrate (Merck, Germany), zinc nitrate (CDH, India), cobalt nitrate (Merck, India) and citric acid (Merck, India). These chemicals were weighed in desired stoichiometric proportions. Iron citrate solution was prepared in deionised water with continuous stirring at 40°C. Solutions of nitrates of Ni, Cu, Co and Zn were also prepared in deionised water, and citric acid was added in 1:1 molar ratio to the metal nitrate solutions. The

resulting metal citrate solutions were heated at 80°C for 30 minutes and then mixed with the iron citrate solution. Ammonia solution was added drop by drop for adjusting the pH of the complex citrate solution to about 7–8 (neutral). The solvent was evaporated at 40°C to obtain the dried citrate precursor. The precursor was calcined at 600°C to obtain the ferrite powder. This powder was compacted by dry pressing in the shape of pellets, which were sintered at 900°C for 3 hours. The ferrite phase formation was investigated by the powder X-ray diffraction technique using a Rigaku (RU 200B) diffractometer. The microstructure was examined using a Cambridge stereoscan 360 scanning electron microscope. Low frequency dielectric measurements were carried out by an LCR meter (Hewlett Packard 4284A), whereas a microwave network analyzer (Hewlett Packard 8719ES) was used for the microwave measurement. A cavity perturbation technique [10] was used for the measurements at microwave frequencies.

Results and discussion

The X-ray diffractograms of the $(\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6})_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x = 0$ and $x = 0.03$) are shown in Fig. 1. The X-ray powder diffraction peaks establish the single-phase cubic spinel structure, and the intense diffraction lines correspond to Ni-Zn ferrite [11]. The lattice parameter ‘a’ has the value 8.45 Å, calculated from the diffraction data. The absence of extra phase formation, generally observed in ferrites synthesized by the conventional ceramic method, indicates that

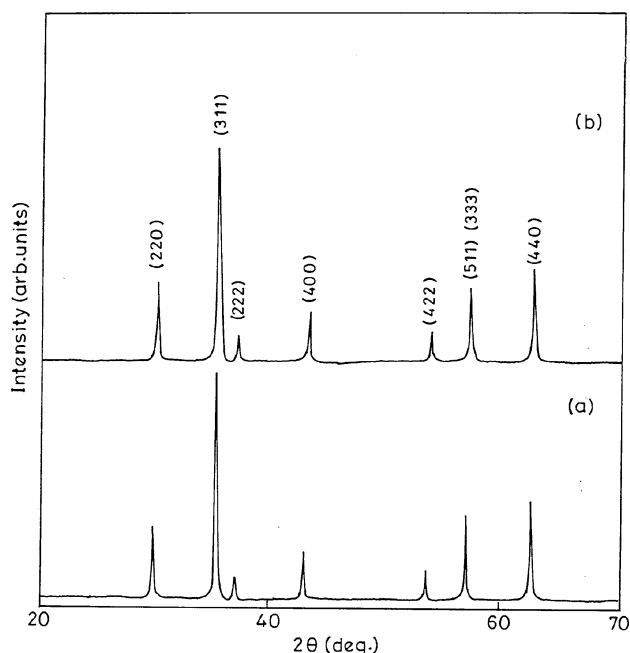


Fig. 1 X-ray diffractograms of polycrystalline $(\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6})_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ samples (a) $x = 0$ (b) $x = 0.03$

the chemical route results in a better quality sample having no impurity phase. This is because in chemical citrate route, the mixing of the cations takes place at atomic level, which results in a very fine, homogeneous and single-phase ferrite formation at lower temperature (600°C). The grain-size in the sintered pellets calculated from the SEM micrographs shown in Fig. 2, were 0.47, 0.70, 0.72, 0.86 μm for the $(\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6})_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ferrite having compositions $x = 0, 0.01, 0.03$ and 0.05 , respectively.

Variation of both the dielectric constant (ϵ') and loss factor ($\tan \delta_\epsilon$) with the low frequencies (50 Hz–1 MHz) are shown in Figs. 3(a) and (b). The values of dielectric constant and loss factor decrease sharply at low frequencies upto 1 KHz, which is because of the interfacial polarization taking place at low frequencies. This can be explained by the model of granular microstructure having grains of low resistivity separated by grain boundaries of high resistivity [8, 12]. The values of ϵ' and $\tan \delta_\epsilon$ are much lower than for the samples prepared by the conventional ceramic method, as reported in the case of Ni-Zn ferrites [13]. The decrease in the values can be explained on the basis of the decrease in Fe^{2+} ions, which are easily polarizable ions. Fe^{2+} ions are easily available in the ferrites prepared by ceramic method because of the sintering at high temperatures. The fine grains resulting from the citrate method and Cu addition reduces the sintering temperature, which results in lowering of Fe^{2+} ions and hence the decrease in the values of ϵ' and $\tan \delta_\epsilon$ as compared to the ferrites prepared by ceramic method.

The compositional dependence of ϵ' and $\tan \delta_\epsilon$ are shown in Figs. 4 (a) and (b). There is no systematic variation in values of ϵ' and $\tan \delta_\epsilon$ with the Co substitution ($x = 0.01$ to $x = 0.05$). The value of ϵ' increases upto $x = 0.03$, and starts decreasing on further Co substitution. The increase in the value of dielectric constant may be attributed to the hopping of the electrons among different cations (available in the system) such as Ni^{2+} , Ni^{3+} , Zn^{2+} , Cu^{2+} , Co^{2+} and Fe^{2+} & Fe^{3+} etc. The hopping of electrons disturbs the octahedral and tetrahedral lattice site positions. This increases the Fe^{2+} ions in the ferrite system, which is more conducting and hence increases the dielectric constant. The values of ϵ' decreases on further increasing Co concentration beyond $x = 0.03$. The values of the dielectric loss ($\tan \delta_\epsilon = \epsilon'' / \epsilon'$) is low for the compositions having $x = 0.01$ and 0.05 and high for the rest of the two compositions. This may be attributed to the crystal inhomogeneity, which affects the losses. SEM micrographs show improved morphology for both the compositions, $x = 0.01$ and 0.05 , as compared to $x = 0$ and $x = 0.03$, resulting in the low losses for these compositions. The losses also depend on the conductivity of ions present in system, which can be explained on the basis of hopping mechanism as already explained in the case of dielectric constant.

The variation of permeability and magnetic loss factor ($\tan \delta_\mu$) is shown in Figs. 5(a) and (b). There is a gradual

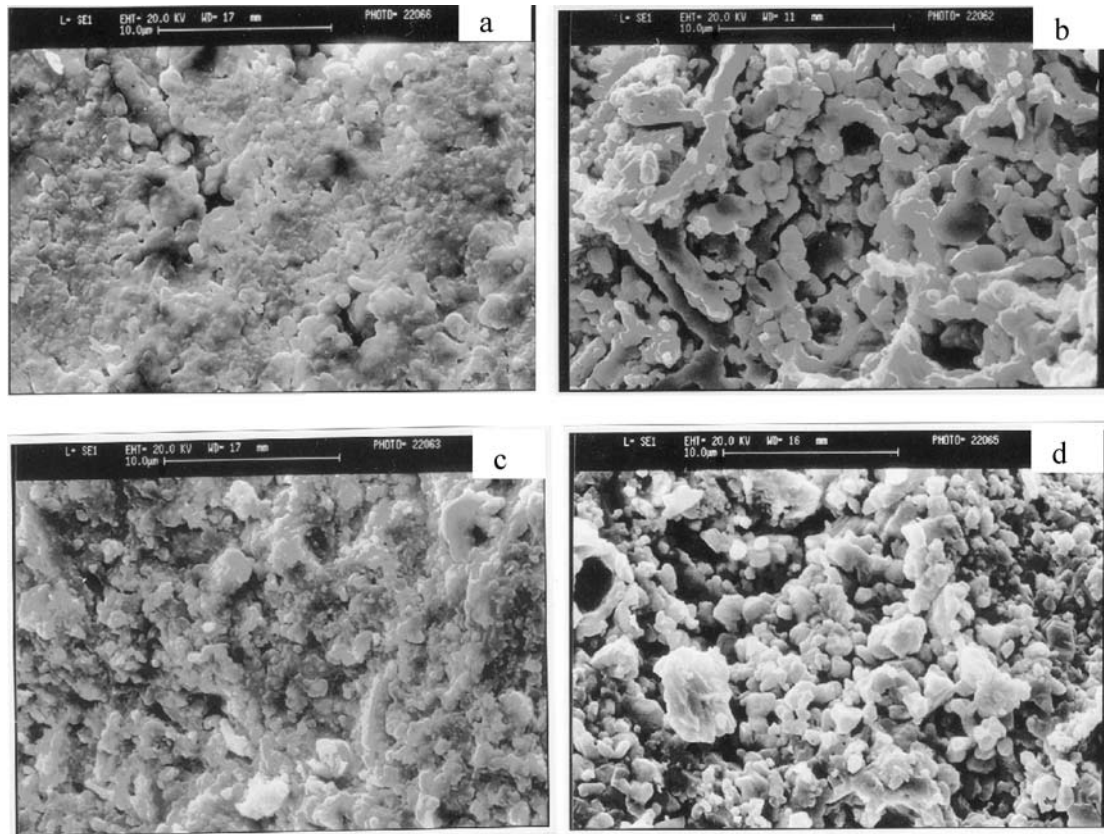


Fig. 2 SEM images of polycrystalline $(\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6})_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ (a) $x = 0$, (b) $x = 0.01$, (c) $x = 0.03$, (d) $x = 0.05$

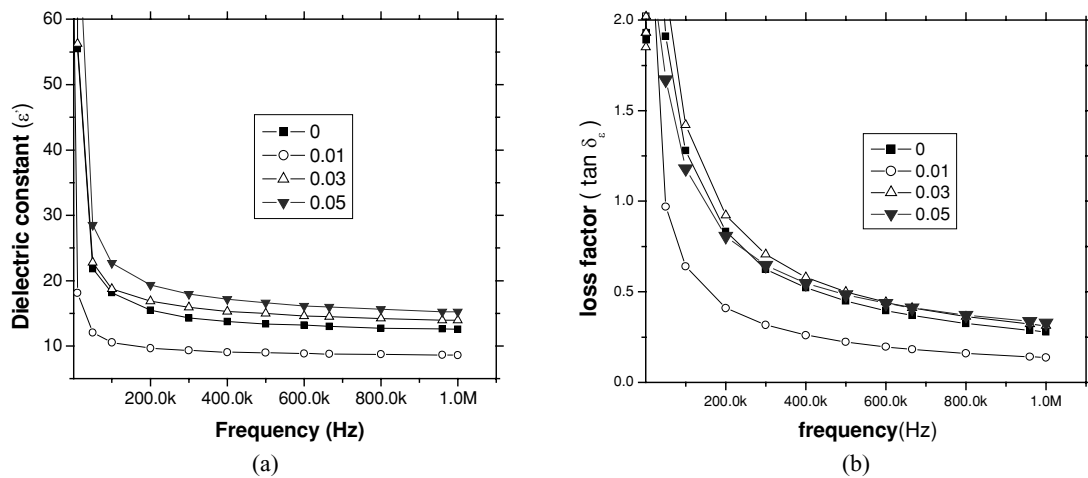


Fig. 3 Variation of (a) dielectric constant and (b) dielectric loss factor of $(\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6})_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ferrite with frequency

increase in the value of μ' at GHz frequencies on increase in the Co concentration ($x = 0.01$ to $x = 0.05$), whereas Byun et al. [6] have reported a decrease in the permeability value at low frequencies with the Co addition. They have explained the decrease on the basis of the intrinsic factors such as saturation magnetization, domain wall motion and anisotropy, because there was not significant variation in the extrinsic properties such as grain size, density etc. But in our case at

GHz frequencies the values of μ' increase with the increase in the Co content. This can be explained by the dependence of μ' on the extrinsic properties, which strongly depends on the preparation method. Magnetic anisotropy decreases on the cobalt addition, which may be one cause of the increase in μ' . This increase in μ' can be a combined effect of decrease in magnetic anisotropy, increase in density and reduction in pores [14]. The permeability of the polycrystalline

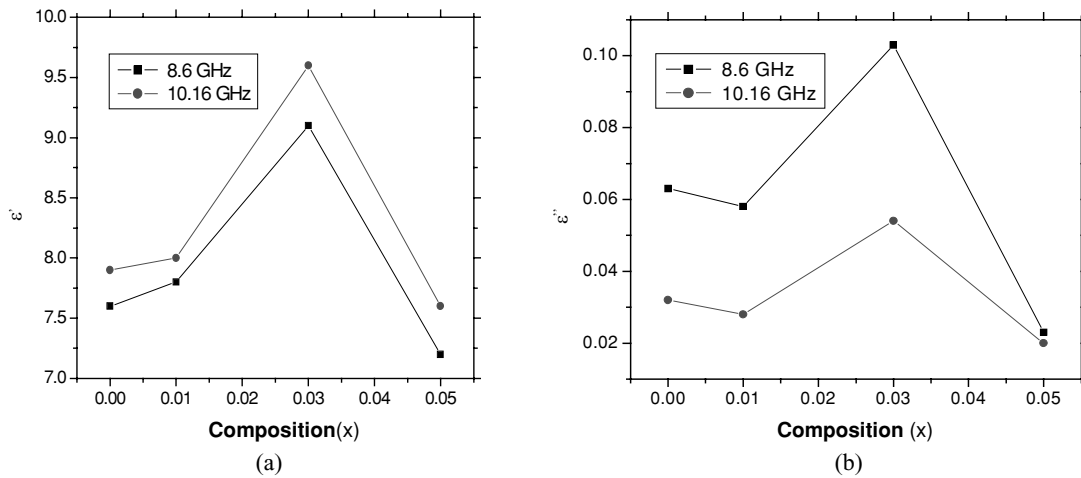


Fig. 4 Variation of (a) dielectric constant and (b) dielectric loss factor of $(\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6})_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ferrite with composition at GHz frequencies

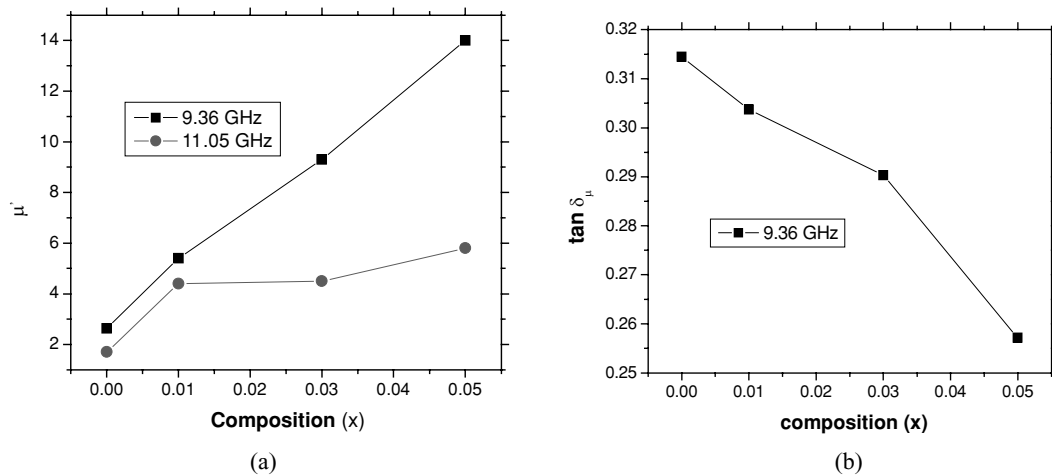


Fig. 5 Variation of (a) permeability and (b) magnetic loss of $(\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6})_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ferrite with composition at GHz frequencies

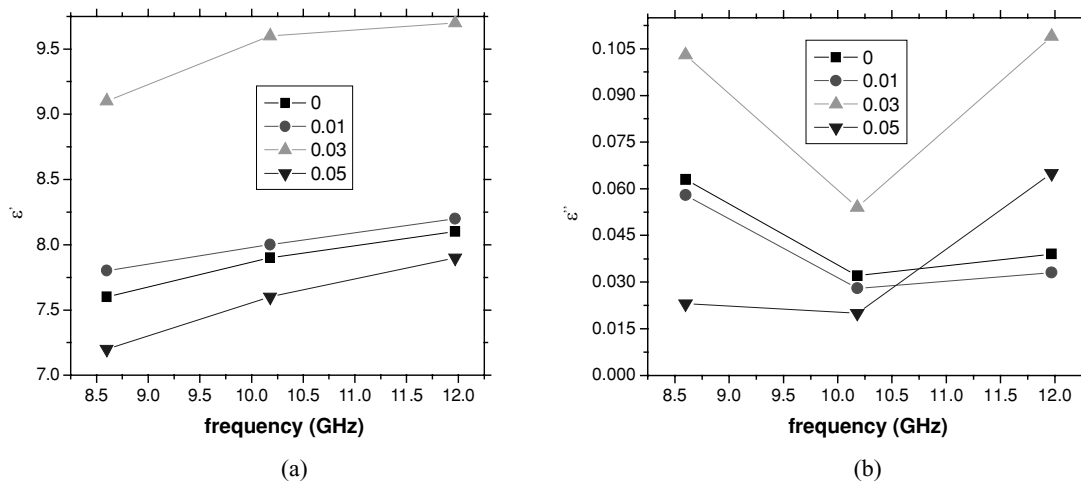


Fig. 6 Variation of (a) dielectric constant and (b) dielectric loss factor of $(\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6})_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ferrite with X-band frequencies

ferrites depends on the domain wall motion and spin rotation [15]. But at high frequencies the main contribution is due to spin rotation, because domain wall contribution is negligible above 50 MHz [16]. The increase in grain size as well as in density of ferrite raises the spin rotational contribution, which in turn increases the value of μ' . The magnetic losses ($\tan \delta_\mu$) also decrease on Co addition, which can be explained on the anisotropy effect, as Ni-Cu-Zn ferrite has negative anisotropy, but Co has '+' ve anisotropy [7], which can neutralize the negative anisotropy effect that results in reduction of the magnetic losses.

Variations of the dielectric constant and loss factor (ϵ' and $\tan \delta_\epsilon$) with the frequencies in X-band are shown in the Figs. 6(a) and (b). There is increase in the values of ϵ' with the increase in the measured frequencies in X-band, which is not normal behavior of ferrites as observed in case of other ferrites, where the values of ϵ' and ϵ'' decreases with the increase in the frequency [17]. The increase in the value of permittivity may be because of the hopping between the cations which increase the conductivity and hence the value of ϵ' . The values of $\tan \delta_\epsilon$ shows a dispersion in the measured frequency range, which may be a second resonance condition, as the first resonance condition in the case of spinal ferrites is below the frequencies of 300 MHz [18]. The resonance condition is caused by the dielectric relaxation process resulting from the hopping and the conductivity mechanisms.

Conclusions

Single-phase $(\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6})_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ferrites were prepared by chemical citrate route at a calcination temperature of 600°C, which is lower as compared to conventional solid-state method. The values of permittivity and permeability strongly depend on the Co concentration. Values of ϵ' and $\tan \delta_\epsilon$ were lower than the values for ferrites prepared by the conventional ceramic method, because of the less number of easily polarizable Fe^{2+} ions due to low temperature sintering.

There is increase in μ' values and decrease in magnetic losses ($\tan \delta_\mu$) at microwave frequencies, because of the combined effect of the intrinsic and extrinsic factors on Co addition. The high values of permeability and low losses at high frequency make this ferrite suitable for the high frequency applications.

Acknowledgments One of the authors, Mukesh C. Dimri, is thankful to Council of Scientific and Industrial Research (CSIR) India, for the financial support.

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