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Dielectric properties of polycrystalline Cu–Zn ferrites at microwave frequencies

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ABSTRACT

The real dielectric constant ε' and complex dielectric constant ε'' of $Cu_{1-x}Zn_xFe_2O_4$ have been measured at room temperature in the high frequency range 1 MHz to 1.8 GHz. At low frequencies the dielectric loss is found to be constant up to 1.4 GHz and there is a sudden rise at 1.5 GHz. A qualitative explanation is given for the composition, frequency dependence of the dielectric constant and dielectric loss of $Cu_{1-x}Zn_xFe_2O_4$. These are correlated with the W–H plot which gives the information about change in the average crystal size and strain of the samples. The micro-morphological features of the samples were obtained by Scanning Electron Microscopy (SEM). The micrograph shows that the increase of the Zn content in Cu ferrite increases the grain size.

1. Introduction

The polycrystalline ferrites are very good dielectric materials and these have occupied a wide range of technological applications. The transport properties of ferrites are very sensitive to the chemical compositions, sintering temperature, sintering time, type and amount of substitution [1]. The studies of dielectric properties of ferrites offer much valuable information on the behavior of localized electrical charge carriers. This leads to a good explanation and also an understanding of the mechanism involved in dielectric behavior of ferrites. The lattice parameter [2,3], Mossbauer [4], and dc electrical conductivity [5], of ferrites have been investigated earlier. The dielectric behavior of Zn with Mg ferrites has been reported by Ravinder and Latha [6]. Microstructure and magnetic behavior of Ni–Fe–O and Ni–Mn–Al–Fe ferrites have been reported by Al-Haj [7]. Electrical conductivity and magnetic properties of Li–Fe–Cr–O ferrites have been reported by Fu [8]. There is a continued interest in the study of frequency and composition dependence of Cu–Zn ferrites on the real part of dielectric constant ε' and dielectric loss $\tan\delta$. The micro-morphological features of Cu–Zn ferrites are studied using SEM and correlated with microstructural parameters.

2. Experimental

The mixed Cu–Zn ferrites having the chemical formula $Cu_{1-x}Zn_xFe_2O_4$ (where $x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) were synthesized by ceramic technique using copper oxide, zinc oxide, ferric oxide (99.9% purity sigma Aldrich). The constituent chemicals were taken in stoichiometric proportion and mixed in the agate mortar for 4 h and then pre sintered in air in an electronically controlled furnace at 1200 °C for 4 h using silica crucible. Then grinding process was repeated before pressing this powder in to disc shaped pellets of diameter of about 1 cm and the thickness ranging from 0.05 cm to 0.1 cm using pallet maker. The pressed samples were annealed at 1000 °C to remove the binder (PVA) and to reduce the porosity of the samples. Later the samples were cooled to room temperature. The dielectric constant and loss of Zn substituted Cu ferrite were measured in the frequency range from 1 MHz to 1.8 GHz using Agilent 4291B impedance analyzer.

X-ray diffraction studies of the samples were performed using CuKα ($\lambda = 1.5418$ Å) (Philips X-pert Diffractometer at IISc Bangalore) radiation. This gives the confirmation of spinel formation. XRD patterns obtained for the samples are shown in Fig. 1.

3. Results and discussion

3.1. Microstructure characterization

From the X-ray diffraction pattern the lattice constant is found to be 8.37–8.44 Å which is in excellent agreement with reported values. Microstructure (crystallite size and lattice strain), especially refers to the packing of the compound at micro-level. The crystallite size dimension increases with the concentration. And it can be explained by the cation radii influence on the crystallite size. The anisotropy due to the crystallite size effects the significant change

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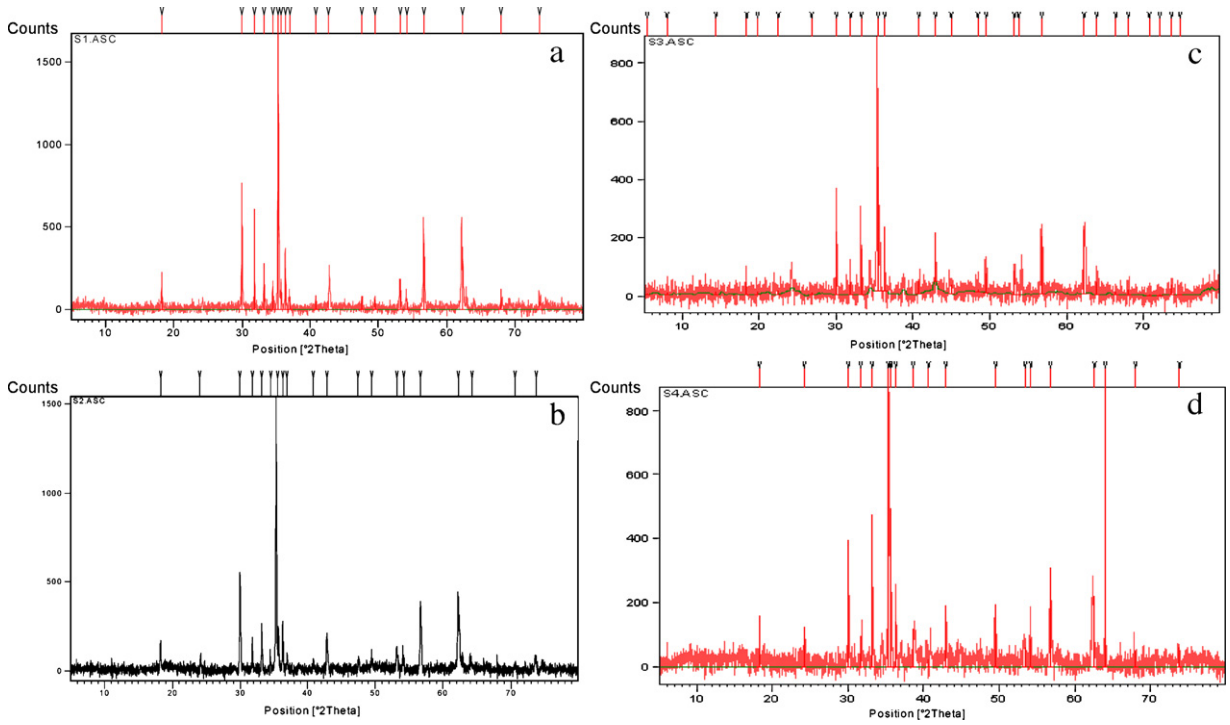

Fig. 1. X-ray patterns of ferrites at different concentrations for Cu–Zn ferrites (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.4$ and (d) $x = 0.6$.

in the dielectric constant. These microstructures play a key role in obtaining the desired dielectric constant of these materials for the microwave applications. The morphology of packing at micro-level is shown in Fig. 2. The surface morphology of all samples as seen from SEM consists of grains varying in size from 109 nm to 219 nm. The grain size increases with the raise in zinc content. This is due to the larger ionic radius of Zn (0.74 Å) compared with Cu (0.68 Å).

3.2. Dependence of dielectric properties on composition

Rezlescu et al. [9] have studied the composition dependence of copper ferrites such as Cu–Mg and Cu–Cr. The dielectric properties of Cu–Cd ferrites have been reported by Kolekar et al. [10]. It has also been reported that a strong correlation between the conduction mechanism and the dielectric behavior of the ferrites [11]. It is also observed that the electronic exchange between Fe^{2+} and Fe^{3+} results in local displacement and hence the polarization of the ferrites. A similar model is proposed for the composition dependence of dielectric constant of mixed Ni–Zn ferrites. In this model the electron exchange is between Fe^{2+} and Fe^{3+} in an n-type and hole exchange between Cu^{3+} and Cu^{2+} in p-type ferrites. These results in local displacement of electrons or holes in the direction of the applied electric field and these electrons determines the polarization. The polarization decreased with increasing frequency and then reaches a constant value due to the fact that beyond a certain frequency of external field the electron hopping cannot fallow the alternating field. This result in agreement with the assumption made by Rabinkin and Novika [12].

3.3. Frequency dependence of dielectric constant (ε')

The variation of dielectric constant as function of frequency in $Cu_{1-x}Zn_xFe_2O_4$ with different composition of Zn is shown in Fig. 3. From Fig. 3, it is observed that the dielectric constant is almost constant up to 1.4 GHz. The dispersion of the dielectric constant is maximum for $x = 0.2$ and decreases as the zinc content is increased. This is possible due to maximum polarization of ions. As the frequency of the externally applied field is increased gradually, though the same number of ferrous ions are present in the ferrite material, the dielectric constant decreases beyond certain frequency. The reason may be due to the exchange of electrons between ferrous and the ferric ions, i.e. $Fe^{2+} \leftrightarrow Fe^{3+}$ may not be in step with the changing field. The variation of dispersion with the composition is also due to the fact that the electron exchange between Fe^{2+} and Fe^{3+} in n-type semiconductor ferrite and hole exchange between Zn^{3+} and Zn^{2+} in p-type semiconductor ferrites. This exchange may have hindrance to the changing electric field beyond a critical frequency.

Fig. 4 shows the variation of loss tangent with frequency for mixed Cu–Zn ferrites. It is observed that in case of $Cu_{0.8}Zn_{0.2}Fe_2O_4$, $\tan\delta$ show maximum at 1.49 GHz and for $Cu_{0.4}Zn_{0.6}Fe_2O_4$ it is at 1.59 GHz. The qualitative explanation for the behavior is due to a strong correlation between the conduction mechanism and dielectric behavior of ferrites [13]. When the hopping frequency of electrons/holes is nearly equal to that of the external electric field, a maximum of loss tangent is observed [14]. From this we infer that this hopping frequency for electrons and holes to be 1.40 GHz and 1.6 GHz, respectively.

The condition for observing a maximum in the dielectric losses of a dielectric material is

$$\omega\tau = 1 \tag{1}$$

where $\omega = 2\pi f_{max}$ and τ is the relaxation time. Now the relaxation time τ is related to the jumping probability per unit time P.

$$\tau = \frac{1}{2P} \tag{2}$$

Eq. (2) shows that f_{max} is proportional to the jumping or hopping probability (P). With decrease in f_{max} with increase in the zinc content, results in decrease of jumping probability per unit time.

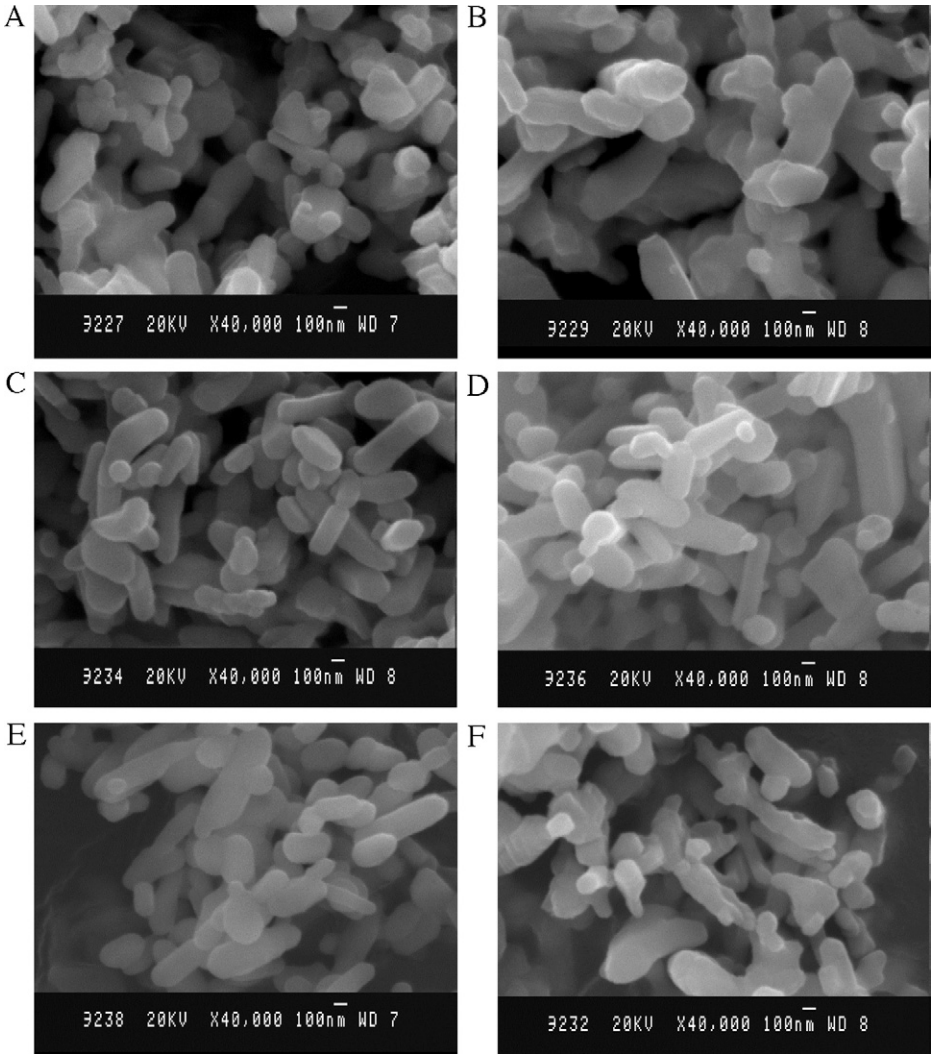

Fig. 2. SEM patterns of Cu–Zn ferrites at different concentrations (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0).

3.4. Crystallite size and micro-strain using Williamson–Hall plot

Changes in the crystallite size and lattice strain in the mixed Cu–Zn ferrite have been studied by recording X-ray powder pattern and employing the Williamson–Hall plot method. If the size and strain broadening is present simultaneously then the crystallite size and strain may be obtained from Williamson–Hall [15,16] plot (Fig. 5). The slope of the W–H plot represents average strain in the samples whereas the intercept on $\beta^*(=\beta\cdot\cos\theta)$ axis gives crystallite size according to the relation

$$\frac{\beta\cdot\cos\theta}{\lambda} = \frac{1}{D} + 4\in\frac{\sin\theta}{\lambda} \quad (3)$$

where β is the full width at half maximum (FWHM), D the average crystallite size and $\in$ the average strain. There is a correlation between the variation of dielectric constant and crystallite size with the increase of Zn in these ferrites. It is evident from Table 1 and Figs. 3 and 4 that there is a plateau region in the range of con-

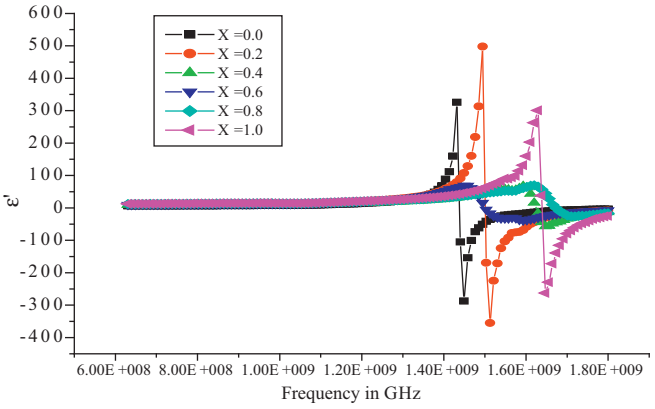

Fig. 3. Permittivity as function of frequency at different concentration for Cu–Zn ferrites.

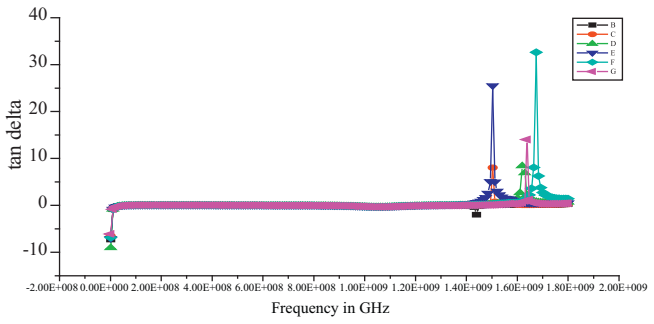

Fig. 4. Dielectric loss tangent of Cu–Zn ferrites at different concentrations.

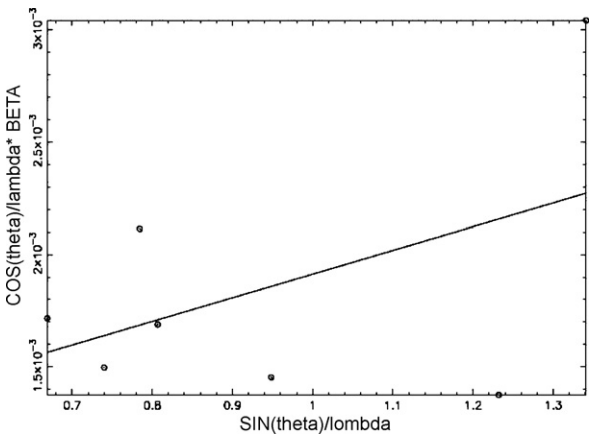

Fig. 5. Williamson–Hall plots to estimate average crystallite size and lattice strain.

Table 1
Micro strain and crystallite size in Cu–Zn ferrites determined using W–H plot.

Samples (composition)	Crystallite size (A)	Microstrain (ε) $\times 10^{-4}$
$CuFe_2O_4$	512.65	7.63
$Cu_{0.8}Zn_{0.2}Fe_2O_4$	570.68	0.79
$Cu_{0.6}Zn_{0.4}Fe_2O_4$	1162.79	10.53
$Cu_{0.4}Zn_{0.6}Fe_2O_4$	436.07	9.42
$Cu_{0.2}Zn_{0.8}Fe_2O_4$	455.17	8.38
$ZnFe_2O_4$	591.55	4.30

centrations $x = 0.2$ to $x = 0.4$ immediately after which one observes extensive decrease in the physical parameters like dielectric constant and crystal strain can be correlated with decrease in crystallite size for some concentration. Essentially, these results emphasis that, maximum dielectric constant is associated with crystalline-like order in Cu–Zn ferrites. Recently, Caruntu et al. [17] have also reported a similar observation in different compounds. It is also evident that the lattice strain decreases with addition of Zn and reaches a minimum corresponding to sample identified as $x = 0.2$ and thereafter the lattice strain increases which is in conformity with the observations made in terms of physical parameters like dielectric constant and loss tangent.

4. Conclusions

The effect of Zn substituted Cu ferrite on the dielectric properties of ferrites were investigated in this study and the results are summarized as follows.

Increase of Zn, in Cu, results in a maximum dielectric constant at an appropriate frequency. Further, the dielectric loss also showed a maximum with frequency. This feature makes these ferrites suitable for high frequency applications. SEM study also gives micro-morphological behaviors of Cu–Zn ferrites. The variation of microstructural parameters like crystallite size and lattice strain with concentration is an indicative of crystalline domain and disorder present in the materials. This kind of disorder also enhances the dielectric constant values in ferrites.

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