COMPLEX PERMEABILITY AND TRANSPORT PROPERTIES OF Zn SUBSTITUTED Cu FERRITES

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ABSTRACT

Zn doped Cu ferrite of the composition $Cu_{1-x}Zn_xFe_2O_4$ ferrites for $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5,$ 0.6 prepared by standard double sintering ceramic technique. SEM micrograph of all the samples revealed that the grain sizes decrease gradually with the increase of Zn content and has great influence on the magnetic and transport properties. Permeability is found to increase with increase in Zn content up to $x = 0.4$ and then slightly decreases with further increase in Zn. The values of relative quality factor (RFQ) changes with Zn concentration. Room temperature DC resistivity changes significantly with Zn addition. The variation of the resistivity versus frequency was studied and the dielectric constant of the system has a variation quite opposite to that of the AC resistivity. Dielectric constant shows the normal behaviour of the ferrite materials that can be explained by the interfacial polarization as predicted by Maxwell and Wagner.

Key words: Microstructure, Initial permeability, Dielectric constant, DC resistivity

INTRODUCTION

Ferrites, a distinct class of magnetic materials known as ferrimagnetic have spinel structure. They consist of spontaneously magnetized domains and show the phenomena of magnetic saturation and hysteresis. The spinel ferrites possess properties of both magnetic materials and insulators and are important in many technological applications (Kingry *et al*. 1976). Their structural, electrical and magnetic properties depend on magnetic interaction and cation distribution in the two sub-lattices, i.e. tetrahedral (A) and octahedral (B) sites. The study of spinel ferrites is of great importance from both the fundamental and the applied research point of view. They have many applications in high frequency devices and play a useful role in technological and magnetic applications because of their high electrical resistivity and consequently low magnetic losses over a wide range of frequency. The spinel ferrite unit cell is based on a closed packed oxygen lattice with two types of cation lattice sites: (1) a tetrahedral lattice site A formed by four oxygen anions and (2) an octahedral lattice site B formed by six oxygen anions (Hu and Mi 2005). The interesting physical and magnetic properties of spinel ferrites arise from the ability of these compounds to distribute the cations among the available tetrahedral (A) and octahedral (B) sites.

The polycrystalline Cu-Zn ferrite could be considered as the most versatile ferrites, due to their high resistivity and low eddy current losses. Generally Cu-Zn ferrites were commercially used in radio frequency circuits, transformer cores, antennas and read

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/write heads for high-speed digital tape and in high quality filters (Calton and Spinu 2001, Maxwell 1982). The present paper reports a complex permeability and transport properties of Cu-Zn ferrite with different Zn concentrations.

Experimental

Samples of the Cu-Zn ferrites having the chemical formula $Cu_{1-x}Zn_xFe_2O_4$ ($x = 0$, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6) were prepared by the standard double sintering ceramic technique using high purity oxides of CuO, ZnO and Fe_2O_3. The reagent powders were weighed precisely according to their molecular weight. The oxides were thoroughly mixed in an agate mortar, heat-treated and compacted in the form of pellets and toroids. During this preparation, pre-sintering at 900°C for 5hours and powdering of the formed products was followed by final sintering at 1000°C for 6hours. The surfaces of all the samples were polished in order to remove any oxide layer during the process of sintering.

The microstructure photographs were taken by Scanning Electron Microscope. For frequency dependence of initial permeability (μ'), the toroids were wound with windings of 5 turns. The inductances were measured over a frequency range of 1 kHz to 13 MHz using a HP4192A impedance analyzer. The initial permeability was calculated using $\mu' = L/L_O$, where L is the measured sample inductance and L_O is the air core inductance using the dimensions of the toroid. The pellet shaped samples were well polished to remove any roughness and the two surface of each pellet were coated with silver paste as contact material for electrical and dielectric measurements. Dielectric measurement and resistivity measurement as a function of frequency in the range 1 kHz-13 MHz at room temperature were carried out using Hewlett Packart impedance analyzer. DC resistivity was measured using an electrometer Keithley model 6514 at room temperature. The experiments were done at Materials Science Divisions, Atomic Energy Center, Dhaka.

Results and discussion

For studying microstructure, the samples were polished by polishing machine using different grade of Al_2O_3 fine powders with water. After fine polishing, they were etched thermally under suitable temperature and observed under SEM. The microstructures of the investigated materials are given in Fig. 1.

Microstructure shows clearly the grain size of ZnO added ferrite is smaller than that of pure $CuFe_2O_4$. This may be explained as due to the fact that the melting point of ZnO (1975°C) (Smit and Wign 1959) is much higher than that of CuO (1325°C) (Maxwell 1982). It means that crystallization of the spinel phase has been aided by CuO. CuO really assists to lower the sintering temperature of CuO added ferrites. Actually CuO acts as fluxing agent in the ferritization reaction (Calton *et al.* 2002). Therefore the role of ZnO in $CuFe_2O_4$ is to stabilize the microstructure i.e. hinders the grain growth during sintering and may has a effect on the magnetic anisotropy, magnetostriction.
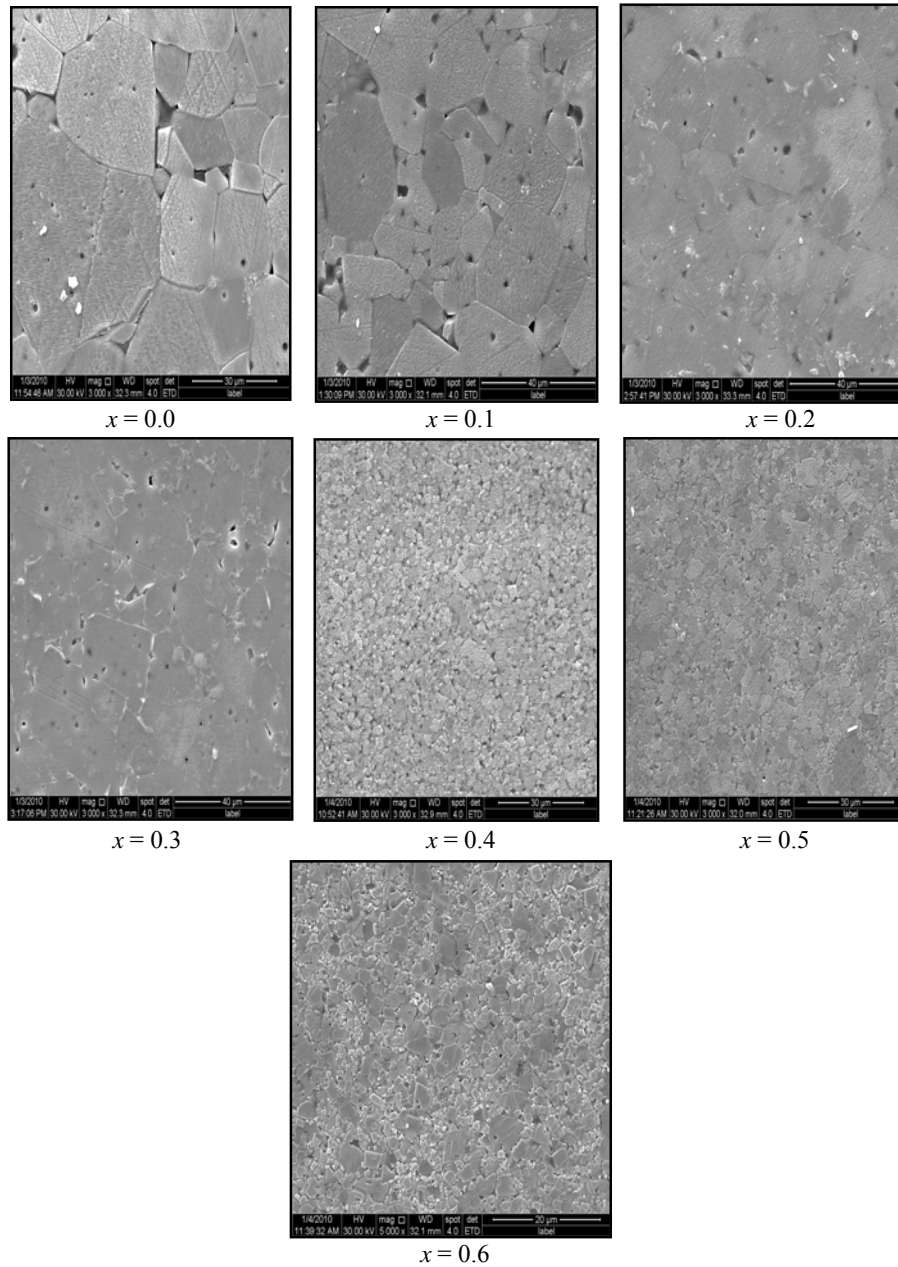
x = 0.0

x = 0.1

x = 0.2

x = 0.3

x = 0.4

x = 0.5

x = 0.6

Fig. 1. Microstructure by SEM of $Cu_{1-x}Zn_xFe_2O_4$ samples sintered at 1000°C.

Initial permeability as dependent on frequency of a magnetic material is an important parameter from the application consideration such as an insulator. Therefore the study of initial permeability has been a subject of great interest from both the theoretical and

practical points of view. The optimization of the dynamic properties such as complex permeability in the high frequency range requires a precise knowledge of the magnetization mechanisms involved. The magnetization mechanisms contributing to the complex permeability, $\mu = \mu' - \mu''$, in soft polycrystalline ferrites have been a controversial subject for a long time and remain unsolved satisfactorily. Although it is admitted that two mechanisms are involved in this phenomenon, the domain wall displacement and the spin rotation in the domains.

Complex permeability has been calculated as a function of frequency up to 13 MHz at room temperature for all the samples of the series $Cu_{1-x}Zn_xFe_2O_4$ ferrites by using the conventional technique based on the determination of the complex impedances of a circuit loaded with toroid shaped sample. Fig. 2 shows the frequency dependent permeability dispersion of ferrites sintered at 1000°C. Initial permeability shows flat profile from 1 KHz to 1 MHz indicating good low frequency stability for the sample with $x = 0, 0.1, 0.2, 0.3, 0.4$ and its dispersion occurs slightly above 1 MHz frequency. But the compositions with values $x = 0.5, 0.6$ shows flat profile above 2 MHz and then dispersion occurs because the domain wall motion plays a relatively important role when the spin rotation reduces.
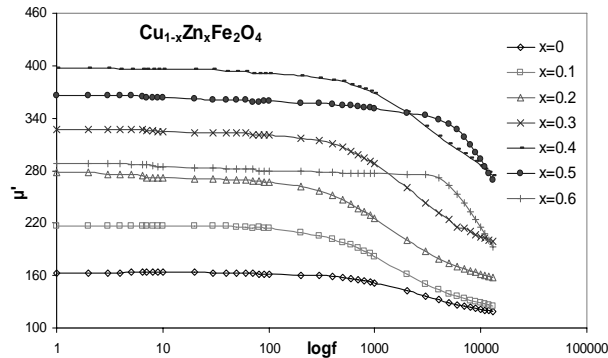

Fig. 2. Real part of permeability (μ′) vs frequency (f) of $Cu_{1-x}Zn_xFe_2O_4$ samples sintered at 1000°C for 6 hours.

It is clearly seen from Fig. 2 that the low frequency permeability increases as Zn content is increased from 0 to 0.4 and decreases with further increase of Zn content. It can be explained that the change of saturation magnetization in Zn substituted Cu ferrite is basically responsible for change in permeability. The basic magnetic properties of $CuFe_2O_4$ system originate from Cu^{2+} ions only in the octahedral B-sites since Fe^{3+} ions are distributed equally in both the A and B-site. The molecular magnetic moment of a mixed ferrite can be increased for a small addition Zn^{2+}. The substituted non-magnetic Zn^{2+} preferentially occupies the tetrahedral A-site replacing an equal amount of Fe^{3+} to octahedral B-sites. This can give rise to an additional magnetization of B-sites. But if the addition of Zn increase is such that x exceeds 0.4, the magnetization of A lattice becomes too small and the A-B interaction weakens. As a result the B-B interaction tends to be

antiferromagnetic. It is to be noted that it is the strong A-B interaction which causes the spins in the B-sites to be aligned parallel. That's why permeability increases when x is up to 0.4 and then decreases when *x* exceeds 0.4. The dependence of permeability on molecular magnetism is such that the force on a domain wall due to a magnetic field and the resultant change of magnetization are both proportional to permeability (Asgar and Manzur 1982, Maria *et al.* 2010).

Fig. 3 shows the imaginary part of the permeability versus frequency spectra of all the samples. The imaginary part associated with loss factor which increases with increase in grain size. For all the samples, the imaginary part of permeability rises rapidly near the resonance frequency. Dispersion or resonance could not be observed in our studied samples since our measurement facility could not be extended beyond 13 MHz. Fig. 4 shows the relative quality factor (RQF), i.e. the ratio of the magnetic loss tangent to the initial permeability. High μ' and low low loss, D i.e. low RQF are required for high frequency magnetic applications. The loss is due to lag of domain wall motion with respect to the applied alternating magnetic field and is attributed to various domain wall defects (Dawoud and Shaat 2006). The results of μ' at 100 kHz for all the samples are demonstrated in table 1 together with the relative quality factor, μ'/D which determines the merit of the magnetic materials from the application point of view. From the loss factor we have calculated the relative quality factor (or μ'/D factor) for all the compositions. The relative quality factors of the prepared samples increase with Zn content and then decreases. This improvement of RQF may be attributed to Zn addition which is expected to the increase of saturation magnetization.
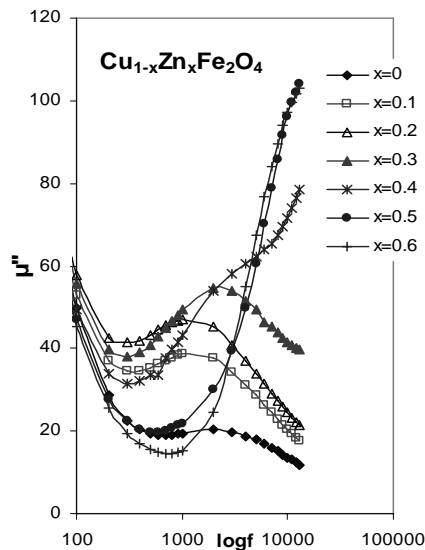

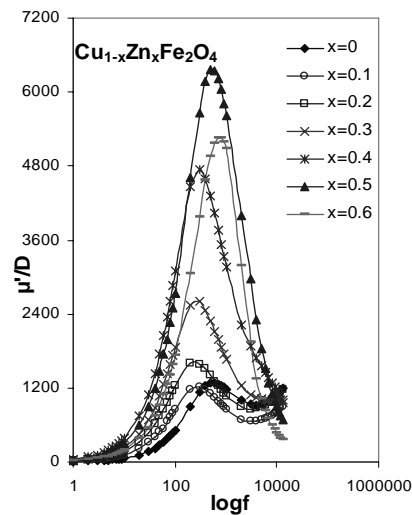Fig. 3. Imaginary part of permeability as a function of frequency of $Cu_{1-x}Zn_x Fe_2O_4$ samples sintered at 1000°C for 6 hours.

Fig 4. Relative quality factor as a function of frequency of $Cu_{1-x}Zn_x Fe_2O_4$ samples sintered at 1000°C for 6 hours.

Fig. 5 shows the variation of dielectric constant with frequency from 10 Hz to 13 MHz at room temperature. The dielectric constant (ε') decreases with increasing frequency, which is rapid at lower frequencies and slower at higher frequencies. At much higher frequency it is very small and becomes independent of frequency. This is a normal dielectric behaviour observed in most of the ferromagnetic materials. The dielectric behaviour of ferrites may be explained on the basis of dielectric polarization process (El Hiti and Abdeen 1998), which is similar to that of the conduction mechanism. The electronic conduction in ferrites is mainly due to hopping of electron between ions of the same element existing in more than one valence state and distributed randomly over crystallographically equivalent lattice sites. A number of such ions formed during the sintering of ferrites. Fe^{2+} ions concentration is a characteristic property of a ferrite material and depends upon several factors such as sintering temperature/time and the grain structure. Creation of Fe^{2+} gives rise to electron hopping between Fe ions in +2 and +3 valence states. The electronic exchange between Fe^{2+} and Fe^{3+} results in local displacement of charges in the direction of applied electric field, which is responsible for the polarization in ferrites (Sawant 1980). The magnitude of exchange depends on the concentration of Fe^{2+}/Fe^{3+} ion pairs present in B-site. The dielectric constant decreases with increasing frequency and then reaches a constant value due to the fact that beyond a certain frequency of external AC field, the electron exchange between Fe^{2+} and Fe^{3+} cannot follow the alternating field. The dispersion is large for samples $x = 0, 0.1, 0.2, 0.3, 0.4$ while samples $x = 0.5, 0.6$ showed a least frequency dependence. The presence of Fe^{2+} ions in excess amount favours the more dispersion. Similarly the weak dependence of dielectric constant on frequency can be due to lack of Fe^{2+}/Fe^{3+} ions concentration.
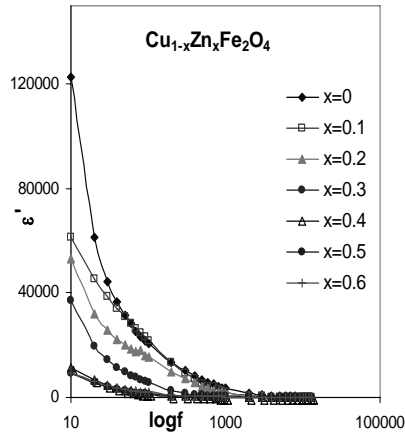

Fig. 5. Dielectric constant (ε') as a function of frequency of $Cu_{1-x}Zn_xFe_2O_4$ samples sintered at 1000°C for 6 hours.
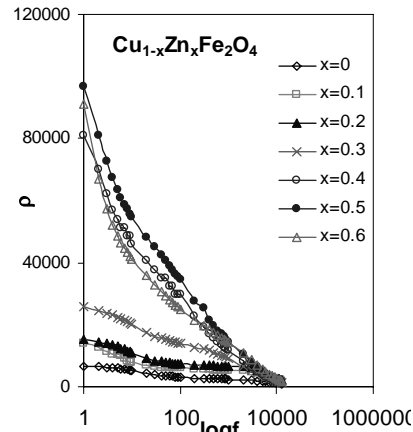
Fig. 6. Resistivity as a function of frequency of $Cu_{1-x}Zn_xFe_2O_4$ samples sintered at 1000°C for 6 hours.

Fig. 5 shows the variation of resistivity as a function of frequency. It is observed from both Fig. 5 and Fig. 6 that resistivity and dielectric constant behaves in an opposite

manner. It is seen from the table 1 that samples with $x = 0, 0.1, 0.2, 0.3, 0.4$ have larger values of resistivity and samples with $x = 0.5, 0.6$ have slightly lower values of resistivity. From microstructure study, we observed that the grain size decrease with Zn content. The smaller grains result in a large no. of grain boundaries which act as the scattering center for the flow of electrons and therefore increase of resistivity (Kingry *et al*. 1976). Table 1 shows the data of DC resistivity at room temperature for all the samples under study. At lower Zn concentration, the increase in DC resistivity is attributed to the hindering of the hopping mechanism between Fe^{2+} and Fe^{3+}. This may be due to the stable bond formation of $Cu^{3+} + Fe^{2+}$ at octahedral sites. The decrease in resistivity at higher Zn content is attributed to the lower concentration of the stable bond of $Cu^{3+} + Fe^{2+}$ (Sawant and Patil 1981). It is also observed that an increase of resistivity may be attributed to the entrapped intra-granular porosity. From the results, it is also determined that the dielectric constant and DC resistivity behaves in an opposite manner.

Table 1. The values of Real part of permeability (μ'), Relative quality factor and DC resistivity of the system $Cu_{1-x}Zn_xFe_2O_4$ sintered at 1000°C for 6 hours.

Zn content x	Real part of permeability, μ' (at f =100kHz)	Relative quality factor, μ'/D	Resistivity P (Ω-cm)
0	161.6228	523.05	5.07×10^3
0.1	214.1673	856.09	8.93×10^3
0.2	266.6117	1234.31	10.89×10^3
0.3	321.1603	1856.42	18.90×10^3
0.4	391.238	3087.91	57.13×10^3
0.5	359.1547	2739.46	52.61×10^3
0.6	279.9308	1727.97	52.62×10^3

CONCLUSIONS

On the basis of the above results and discussion, the following conclusions can be drawn:

(1) Microstructures of the samples have great influence on the magnetic and transport properties.

(2) The increase of low frequency permeability of Cu-Zn ferrites with Zn addition up to $x = 0.4$ is due to the increase of magnetization of B-sites. But further addition of Zn causes the A-B interaction to be weak. As a result B-B interaction tends to be antiferromagnetic and the permeability decreases.

(3) The relative quality factors of the prepared samples increase with Zn content and then decrease. This improvement of RQF may be attributed to Zn addition which is expected to the increase of saturation magnetization.

(4) Ferromagnetic materials show the normal dielectric behavior.

(5) Room temperature DC resistivity increases with Zn content and behaves in an opposite manner with the dielectric constant.

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