Journal of Thermal Analysis, Vol. 37 (1991) 2465-2471

MECHANICAL AND ELECTRICAL PROPERTIES OF $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ FERRITE

M. I. Abd El-Ati and A. Tawfik

PHYSICS DEPARTMENT, FACULTY OF SCIENCE, TANTA UNIVERSITY, TANTA, EGYPT

(Received January 5, 1991)

A series of samples in the system $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ (x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5) were prepared by the usual ceramic technique. X-ray analysis showed that they were cubic spinel (single phase). Young's modulus, the dielectric loss and the change in capacitance under mechanical stress were measured for the samples. Young's modulus decreased with increasing Cu content. This is due to the fact that Cu^{2+} ions entered the lattice substitutionally for Fe^{3+} ions at the octahedral sites, creating lattice vacancies gave rise to lattice strain.

The minimum value of the dielectric loss corresponding to $x = 0.3$ may be due to the formation of lattice vacancies retarding the jump frequency to be far from the frequency of the applied a.c. field.

The increase in capacitance of the samples with mechanical stress may be explained via the mechanism of dielectric polarization.

1 Introduction

The recent development of a high-magnetization nickel-zinc ferrite with stress-insensitive square hysteresis loop, achieved through substitution of Mn^{3+} ions, has prompted a study of the family $Fe^{3+}_{0.65}Zn^{2+}_{0.35}[Ni^{2+}_{0.65}Fe^{3+}_{1.35-x}Mn^{3+}_x]O_4$. The magnetic and dielectric properties of compositions with x ranging from 0 to 0.4 were measured to determine the effects of manganese substitution over this concentration range. As anticipated, the saturation magnetization gradually decreased with increasing x, because of the reduced magnetic moment in the B sublattice of greater importance [1].

In studies of the dielectric behavior of Ni-Zn ferrites, a low-frequency dispersion of the dielectric constant has always been reported [2–8].

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Typically [3], this dispersion begins at $\simeq 10^5$ Hz, with the dielectric constant (16 at 10^3 Hz) increasing rapidly in the audio-frequency range to relatively large values (1980 and apparently still rising) at the lowest frequency of observation (160 Hz). Indeed, 'the low-frequency level for ε has never been reached' [6]. The dispersion is strongly influenced by the firing conditions used in preparing the ferrite, and dielectric constants from 1710 to 39.000 at 1000 Hz have been reported [3]. In another investigation [7], the low-frequency data were extrapolated downward from 200 Hz, and low-frequency limits for the dielectric constant of 2500 to 21.800 were given.

Koops [3] described the dispersion by assuming that the sintered ferrite is made up of ferrite grains separated at the grain boundaries by thin layers of a substance of relatively poor conductivity. This model was represented by an electrical circuit in which two capacitors in series were considered to be equivalent to the ferrite dielectric. By choosing appropriate constants (including two relaxation constants), the experimental data were approximated. Subsequent work [7, 9] has elaborated on Koop's descripton.

The dielectric behavior of Ni–Zn ferrites was investigated in light of recent work [10, 11] which showed that these ferrites have unusually high resistivities and products $\mu_o Q$ when they are stoichiometric with respect both to oxygen and to a 1:1 molar ratio of the divalent oxides to Fe_2O_3. Another reason for reopening the subject is that the conditions for preparing these stoichiometric compositions are especially critical e.g. a 0.1 % deviation in mol% Fe_2O_3 from 50% or a firing temperature 30 deg different from that for equilibrium between the ferrite and the partial pressure of O_2 in the air will produce a 1000–fold reduction in resisitivity. It therefore seemed that these conditions for preparing the stoichiometric compositions may not have been met in earlier work.

In the present investigation, a study has been made of the mechanical and electrical properties of $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ (x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5), including the effect of stress on the dielectric constant and the dielectric loss, and the effect of x on Young's modulus.

2 Experimental procedure

A series of samples in the system $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ (x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5) were prepared by the usual ceramic technique. The samples were pressed into discs, sintered at 1200° for 8 h, and slowly cooled by switching off the furnace. X-ray diffraction showed that the prepared samples are cubic spinels (single phase). The discs were polished and covered by silver paste as a contact material. The dielectric constant ε' and the d.c. conductivity σ_{dc} of the prepared samples were measured at a frequency of 1 KHz, using an RLC bridge type BM 591. The measurements were carried out at room temperature.

3 Results and discussion

3.1. Effect of Cu additions on the Young's modulus of $Ni_{0.65}Zn_{0.35}Fe_2O_4$ *ferrites*

The variation of Young's modulus *Y* as a function of copper additions *x* in $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ is represented in Fig. 1. It is seen that Young's modulus decreased with increasing Cu content; it attained a maximum value at $x = 0.3$ and then decreased for $x > 0.3$

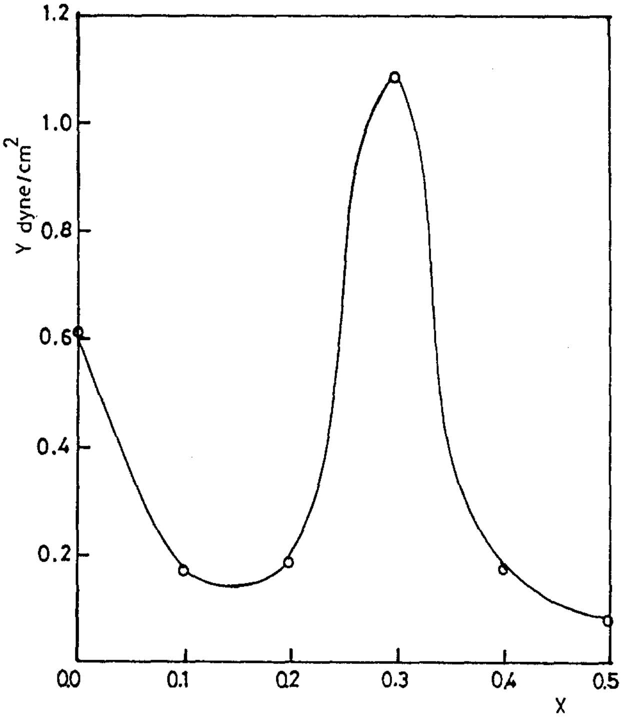

Fig. 1 Variation of Young's Modulus of $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ ferrite with Cu additions (*x*)

Our results are explained on the assumption that Cu^{2+} ions enter the lattice substitutionally for Fe^{3+} at octahedral sites for $x < 0.3$ in

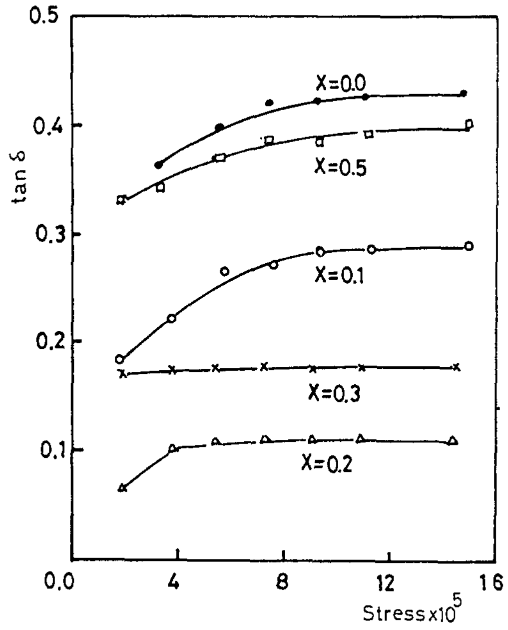

Fig. 2 Effect of stress on the dielectric loss for different x.

$Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$. The introduction of Cu^{2+} ions into the lattice results in a decrease in the number of Fe^{3+} ions at octahedral sites, which increases the lattice strain. This is because the introduction of Cu^{2+} ions created lattice vacancies [12], which give rise to lattice strain under external mechanical stress. For increasing x up to 0.3, the oxygen vacancies accelerate densification during sintering [13]. The pronounced increase in the density of the ferrite [12] minimizes the lattice strain, leading to high Y. For $x > 0.3$, the decrease in Young's modulus is explained on the assumption that the enhanced substitution of Cu^{2+} ions for Fe^{3+} ions created cation vacancies, which reduced the anion vacancies, with a decrease in the density of the composition. The decrease in density increased the lattice strain under the external mechanical stress.

3.2. Variation in dielectric loss with mechanical stress

The variation in the dielectric loss (tan δ) with mechanical stress for $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ is shown in Fig. 2. The increase in the dielectric loss (tan δ) with mechanical stress up to $6 \cdot 10^5$ dyne/cm^2 can be explained by the increasing hopping frequency between the holes for the p-type [12] of

$Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ to approach the frequency of the external electric field [14]. For higher stress, the jumping frequency is saturated to the optimum value near the frequency of the applied field.

3.3 Effect of copper additions on dielectric loss of $Ni_{0.65}Zn_{0.35}CuxFe_{2-x}O_4$

The effect of Cu^{2+} additions on the dielectric loss is shown in Fig. 3. A minimum value was attained near $x = 0.3$. It has been suggested that the substitution of Cu^{2+} ions into $Ni_{0.65}Zn_{0.35}Fe_2O_4$ might cause the formation of vacancies. However, if excess vacancies are formed, these would be anion vacancies rather than cation vacancies, since the Cu^{2+} ion has a lower charge than the Fe^{3+} ion. These vacancies retard the jumping frequency, which is far from the frequency of the applied a.c. field.

For higher additions, the reduction of anion vacancies by the generation of cation vacancies retards densification during sintering of the samples, which increases the porosity of the samples. The existence of the pores gives rise to scattering, which causes an increase in the dielectric loss.

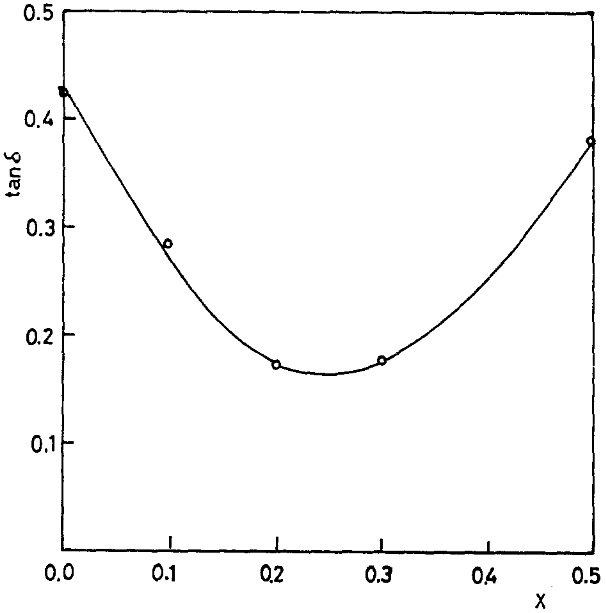

Fig. 3 Variation of tan δ with x at stress 10^5 dyne/cm^2

3.4. Effect of Cu_{2+} additions on capacitance of $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$

The variation in the change of capacitance with mechanical stress is shown in Fig. 4. The increase in the capacitance of the samples with mechanical stress is explained as follows: the mechanism of dielectric polarization is similar to that of conduction [15]; It was observed that the electron exchange interaction $Fe^{2+} \leftrightarrows Fe^{3+}$ determines the polarization of the ferrites. In our case, when stress is applied, the change in the charge on the electrode is

$$\frac{\partial Q}{\partial \sigma_1} = A \cdot \frac{\partial P}{\partial \sigma_1} + P \cdot \frac{\partial A}{\partial \sigma_1}$$

where Q is the charge on the electrodes, P is the polarization in charge per unit area, A is the area of the electrodes and σ_1 is the stress [16].

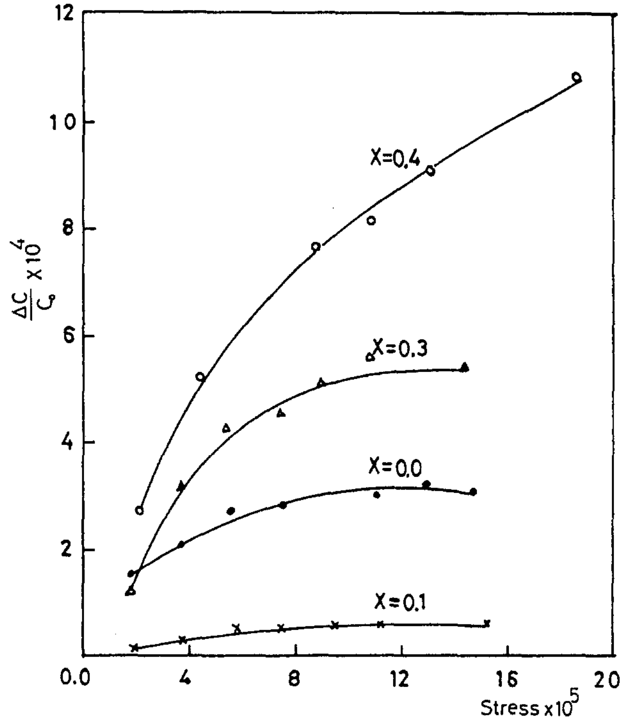

Fig. 4 Effect of mechanical stress on the capacitance of $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ ferrite

Thus, the displacement of Fe^{3+} ions at the octahedral sites results in a local displacement of electrons in the direction of the plays a dominant role in the mechanism of the dielectric polarization. Further, the electron exchange interaction $Fe^{2+} \leftrightarrows Fe^{3+}$ at the octahedral sitesresults in a local displacement of electrons in the direction of the mechanical stress, giving rise to more polarization. The increase in polarization increases the capacitance of the samples.

References

1 G. Dionne and R. West, J. Appl. Phys., 61 (1987) 3868.
2 D. Polder, Proc. Inst. Elec. Eng., A, 97 (1950) 246.
3 C. G. Koops, Phys. Rev., 83 (1951) 121.
4 A. Fairweather and E. J. Frost, Proc. Inst. Elec. Eng., A, 100, (1953) 15.
5 L. G. Van Uitert, Proc. IRE 44(10) (1956) 1294.
6 J. Smit and H. P. W. Wijn, Ferrites, Philips Technical Library, Eindhoven, Netherlands 1959, pp. 236-42.
7 M. Kroetzsch, Phys. Status Solidi, 6 (1964) 479.
8 G. Dietzmann, M. Kroetzsch and S. Wolf, Phys. Status Solidi, 2 (1962) 1762.
9 P. H. Fang, Phys. Status Solidi, 9 (1965) 793.
10 F. G. Brockman and K. E. Matteson, J. Amer. Ceram. Soc., 53 (1970) 517.
11 F. G. Brockman and K. E. Matteson, J. Amer. Ceram. Soc., 53 (1970) 180.
12 S. A. Olofa, A. Tawfik, M. H. Henaish and M. M. Barakat, under publication.
13 E. C. Subbarao, J. Amer. Ceram. Soc., 43 (1960) 119.
14 V. R. K. Moorthy and J. Sobhanadri, Phys. Status Solidi A, 36 (1976) K 133.
15 L. I. Rabinkin and Z. I. Novikova, Ferrites, Minsk 1960 p. 146.
16 R. G. Kepler and R. A. Anderson, J. Appl. Phys., 49 (8) (1978).

Zusammenfassung — Mittels herkömmlicher keramischer Techniken wurden eine Reihe von Proben im System $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ ($x = 0.0$, 0.1, 0.2, 0.3, 0.4 und 0.5) hergestellt. Die röntgenographische Analyse zeigte für alle Proben ein kubisches Spinell (Single-Phase). An den Proben wurde das Elastizitätsmodul, der dielektrische Verlust und die Kapazitätsänderung bei mechanischen Einflüssen gemessen. Das Elektrizitätsmodul sank mit zunehmenden Kupfergehalt. Dies hängt mit dem Fakt zusammen, daß Fe^{3+} Ionen im Gitter an oktaedrischen Punkten durch Cu^{2+} Ionen ersetzt werden, was Gitterleerstellen verursacht, die die Gitterspannung erhöhen.

Das Minimum des dielektrischen Verlustes für $x = 0.3$ kann mit der Bildung von Gitterleerstellen erklärt werden, was die Sprungfrequenz weitab von der Frequenz des angewendeten Wechselstromfeldes hält.

Die steigende Kapazität der Proben bei mechanischem Einfluß kann über den Mechanismus der Polarisation erklärt werden.