Journal of Thermal Analysis, Vol. 37 (1991) 605-611

ELECTRICAL PROPERTIES OF $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ FERRITES

M. A. Henaish, S. A. Olofa, M. M. Barakat and T. Tawfik

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

(Received August 21, 1990)

A series of samples in the system $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ ($x = 0$, 0.1, 0.2, 0.3, 0.4 and 0.5) were prepared by the usual ceramic technique. Seebeck coefficient, d.c. resistivity, activation energy, drift mobility μ and time constant measurements are presented for all samples. As expected, the activation energies were lower for samples of higher conductivity and mobility.

Ferrites have a very low conductivity, which is one of the considerations for microwave applications. The electric resistivity of ferrites at room temperature depends upon the chemical composition [1]. The electric conduction mechanism of ferrites containing Fe^{2+} ions was explained by the hopping motion of electrons between Fe^{2+} and Fe^{3+} ions at the octahedral sites of the spinel lattice [2].

The activation energy, resistivity and Seeback coefficient were earlier measured for a semiconducting $CoFe_2O_4$ [3]. It was found that the charge carriers are not free to move through the crystal lattice, but jump from ion to ion. The resistivity for ferrites decreases with increasing temperature. A series of samples in the system $Co_{1-x}Zn_xFe_2O_4$ (x = 0.3, 0.4, 0.6, 0.8 and 1) was prepared by the usual ceramic technique [4]. Thermopower and d.c. resistivity measurements were carried out and the drift mobility μ at different temperatures was calculated. The activation energies and the d.c. conductivity σ for different samples are presented. The activation energies are lower for samples of higher conductivity.

In this paper, the resistivity, activation energy, Seebeck coefficient, time constant and mobility are calculated for different samples in the system $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5).

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

Experimental

Sample preparation

Samples in the system $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5) were prepared by using the usual ceramic technique. The pure oxides were mixed and then ground to a very fine powder in a carborundum mortar. Samples in the form of discs were sintered at 1200° for 8 h and slowly cooled to room temperature. The samples were polished so as to have uniform parallel surfaces. Contacts on the sample surface were made with silver paste for electrical measurements. The X-ray diffraction pattern for each sample was recorded with a Philips X-ray diffractometer of type PW 1729. It showed that the prepared samples are cubic spinel.

Measurement

The d.c. resistivity measurements on the ferrites were carried out with an automatic TESLA RLCG bridge of type BM591. Temperature was measured with a KEITHLEY 871 digital thermometer of type K Tc to an accuracy of 0.1 deg. The capacitance of the samples was measured with the same bridge.

The temperature dependence of the thermoelectric power α was measured with NiCr-Ni thermocouples. The sign of the thermovoltage was determined from the polarity of the cold end of the specimen, as the charge carriers diffuse from the hot to the cold part. The thermovoltage divided by the temperature difference gives the thermoelectric power. Details of the apparatus used are given elsewhere [5].

Results and discussion

Electrical conductivity in $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ ferrites

The variation of the conductivity with temperature in the temperature range 15-250° for all ferrites is shown Fig. 1. A marked change in the slope is observed. The change in the slope may be due to a change in the conductivity mechanism [6]. The actiation energies are calculated from the formula

$$\sigma = \sigma_o \exp\,(-E/RT),$$

where E is the activation energy, K is the Boltzmann constant, and T is the absolute temperature. The results are shown in Fig. 2. It is observed that the low activation energy for $x = 0.4$ causes the pronounced increase in the d.c.

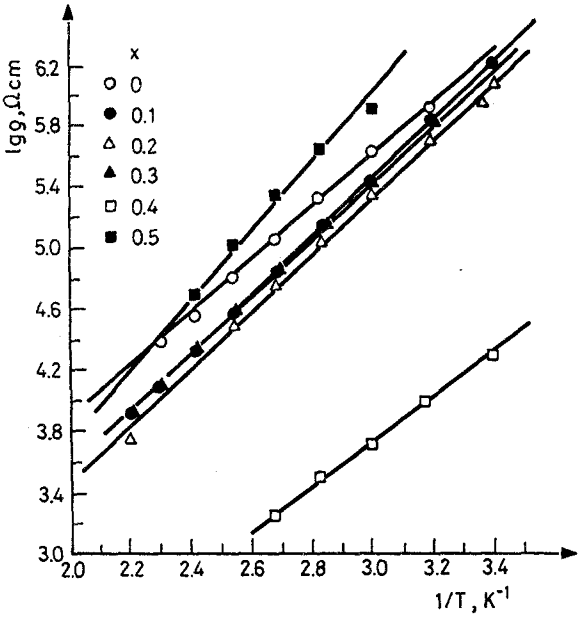

Fig. 1 The variation of (log ρ) as a function of $(\frac{1}{T})$ for x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5

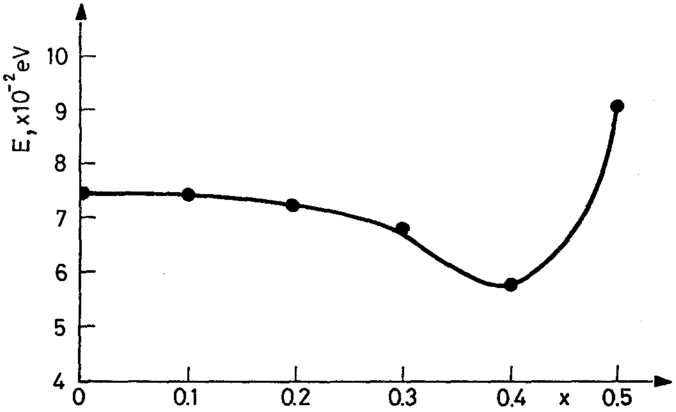

Fig. 2 The variation of activation energy E(eV) as a function of x

conductivity. From our results, the conductivity increases as the temperature is elevated, due to the generation of more holes (p-type conductivity) as previously reported by the present authors [7]. The decrease in the activation energy on Cu addition may be due to the fact that the introduction of Cu^{2+} into the lattice creates lattice vacancies. Since the valency of Cu^{2+} is less than the valency of Fe^{3+}, more oxygen vacancies will be formed [7], which give rise to conductivity and decrease the activation energy. At $x > 0.4$, the increase in the activation energy and the decrease in the conductivity are attributed to the creation of more cations which reduce oxygen vacancies. The trend of these results is similar to that in previous work [3, 8], which demonstrated a decrease in resistivity with increasing temperature for ferrites.

Effect of temperature on the Seebeck coefficient for different compositions

The effect of temperature on the Seebeck coefficient for the different compositions is shown in Fig. 3. The compositions containing Cu additives have a positive value of the Seebeck coefficient α. The explanation of this behaviour was discussed previously by the authors [7].

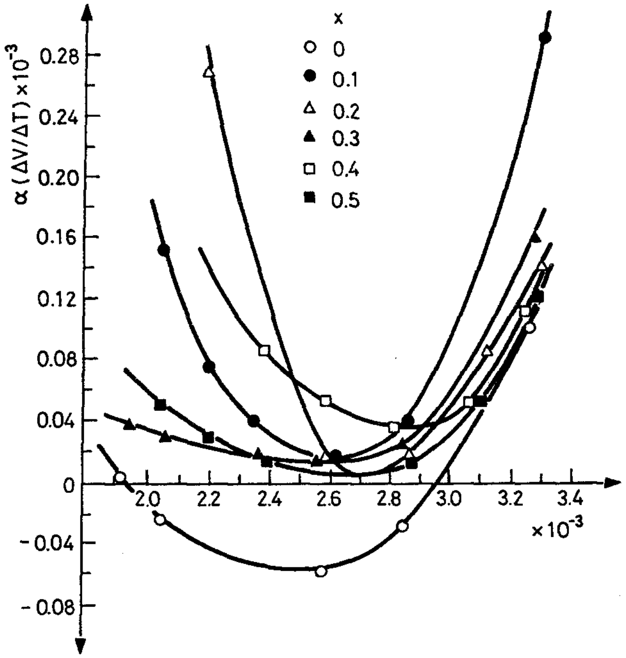

Fig. 3 The variation of Seebeck coefficient α as a function of $\frac{1}{T}$ (K–1) for different samples

Effect of copper additives on the mobility of charge carriers

The mobility of charge carriers was estimated from the following equation:

$$\mu = \frac{1}{nep}$$

where μ is the drift mobility and n is the concentration of charge carriers, and can be calculated from $n = cN$, where N, is the number of iron atoms at the octahedral sites; $N = 1.35 \cdot 10^{22}$ atoms/cm^3 for the cubic spinel lattice, and c represents the concentration of Fe^{2+} ions at the octahedral sites. The transport theory of strongly localized carriers has been developed for small polarons. In the case of hopping of polarons of small radius [2], the expression for α is

$$\alpha = \frac{2.3K}{e} \log \frac{1-c}{c}$$

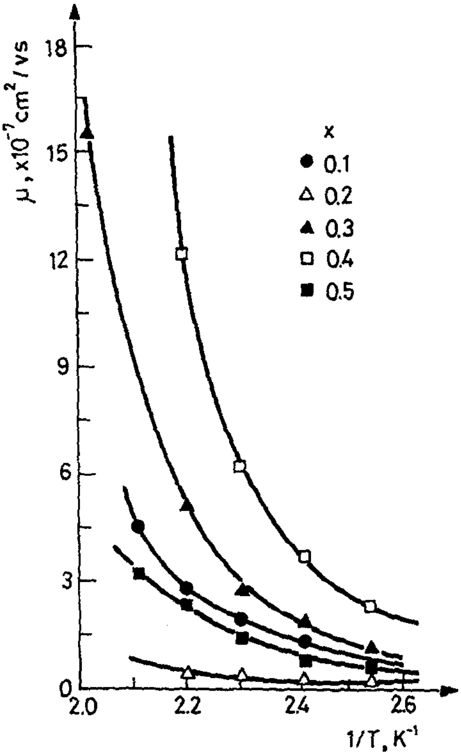

Fig. 4 The variation of drift mobility μ_p as a function of $\frac{1}{T}$ for different samples

where K and e are the Boltzmann constant and the electronic charge, respectively.

The drift mobility values for p-type charge carriers μ_p, as a function of the composition ration x in $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5), are shown in Fig. 4. The values of the drift mobility in the paraelectric state ranged from $0.2 \cdot 10^{-7}$ to $16 \cdot 10^{-7}$ cm^2/vs. We can discuss the mobility results in the light of the conductivity values; the high values of conductivity in the sample $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ explain the high mobility at $x = 0.4$. A low activation energy value corresponds to a higher mobility. This energy is required for the hole to hop. The effect of temperature on the mobility is in agreement with the findings in previous work [9-12].

Effect of copper additives on the time constant

The effect of Cu^{2+} on the time constant of our samples is shown in Fig. 5. The decrease in the time constant with increasing x at room temperature is attributed to the creation of oxygen vacancies due to the introduction of Cu^{2+} ions into the lattice.

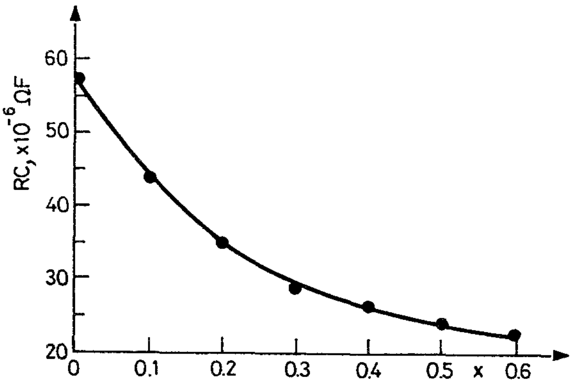

Fig. 5 The variation of time constant RC as a function of x

* * *

The authors express their thanks to the technical staff of the Central Laboratory of Tanta University for providing X-ray diffraction patterns.

The electrical measurements were carried out at the Solid-State Physics Laboratory, Faculty of Science, Tanta University, Egypt.

References

1 E. J. W. Verwey, P. W. Haaijman, F. C. Romeym and G. W. Van Oosterhout, Philips Res. Rep., 5 (1950) 173.
2 I. G. Austin and N. F. Mott, Adv. Phys., 18 (1969) 41.
3 F. G. Brockman and K. E. Matteson, J. Amer. Ceram. Soc., 53 (1970) 517.
4 M. A. Ahmed, Phys. Stat. Sol., (a) 111 (1989) 567.
5 A. A. Ghani and M. A. Ahmed, Proc. Math. Phys. Soc. Egypt, 12 (1976)
6 K. R. Krishna Murthy, Ph. D. Thesis I. I. T. Madras 1975.
7 S. A. Olofa, A. Tawfik, M. A. Henaish and M. M. Barakat, under publication
8 O. S. Josyulu and J. Sobhanadri, Phys. Stat. Sol., (a) 59 (1980) 323.
9 G. I. Epifanov, Solid State Physics, Izd. Mir, Moscow 1979, p. 180.
10 F. J. Morin, Phys. Rev. 93 (1954) 1195.
11 F. J. Morin, Phys. Rev. 93 (1954) 1199.
12 A. A. Samokhvalov and A. G. Rustamov, Soviet Phys. Solid State 7 (1965) 961.

Zusammenfassung — Mittels keramischer Techniken wurde eine Reihe von Proben des Systemes $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-4}O_4$ (mit x = 0, 0.1, 0.2, 0.3, 0.4 und 0.5) hergestellt. An allen Proben wurden Messungen von Seebeck Koeffizient, Gleichstromwiderstand, Aktivierungsenergie, der Driftbeweglichkeit und von Zeitkonstanten durchgeführt. Wie erwartet, liegt die Aktivierungsenergie bei höherer Leitfähigkeit und Beweglichkeit der Proben niedriger.