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Thermoelectric energy conversion of Cu doped ferrite

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Abstract

The Tawfik constant indicates the type of conduction in Cu doped Ni–Zn ferrite in the ferromagnetic state. This constant assumes more positive values with increasing Cu additions, causing p-type conductions at the B sublattice. The thermoelectric field (pyroelectric field) has been studied as a function of temperature. It increases with temperature because of increasing hopping of holes for positive values of the Tawfik constant. The increase of hole hopping increases the pyroelectric coefficient. The findings are of interest for obtaining pyroelectric materials for thermoenergy conversion.

INTRODUCTION

The idea of using the pyroelectric effect for the conversion of heat to electrical energy has been the subject of renewed investigation recently. Some authors are now suggesting that this type of conversion may be much more efficient than previously believed [1,2]. In addition, generators have been built [3,4] which produce over a thousand times the power of the machines of the 1960s. In the light of such developments it seems appropriate to investigate the electrical generation properties of a particularly attractive pyroelectric material [5].

General discussions of pyroelectric energy conversion may be found elsewhere [6–10]. Detailed descriptions of the advances in this field have also appeared [11,12]. Measurements of polarization versus applied electric field have been made on specimens of lead zirconate modified with Sn^{4+} and Ti^{4+} as a function of temperature [13]. The authors estimated the amount of hysteretic loss which may be encountered in heat-to-electrical conversion using this ferroelectric, and also analyzed the sensitivity of the electrical energy output to the operating temperature.

The aim of the present work is to investigate the magnitude of the electric field produced over variations in the operating temperature and the Cu additions x for $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ ferrites and also to establish how sensitive the pyroelectric coefficient γ is to the variations in temperature and x.

EXPERIMENTAL

A series of samples of 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) was prepared by the usual ceramic technique. The samples were pressed into discs, sintered at 1200°C for 8 hours, and slowly cooled to room temperature 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 apparatus used for the pyroelectric measurements is shown in Fig. 1. It comprises a sample holder (1) held on three iron rods (2). The sample holder consists of a stainless steel bar (3) which is fixed in the central axis of an internal and an external furnace (4, 5), each of which is provided with a heater. The two heaters and the stainless steel bar are fixed to the holder base. The central steel bar, copper leads, thermocouple wire and heater connections are insulated from the holder base plate by a ceramic disc (6). Connecting wires and thermocouples pass through ceramic tubes and lead to the outside through Teflon tubes (7) in the apparatus base plate by means of copper leads (8). The sample *s* is tightly pressed between two

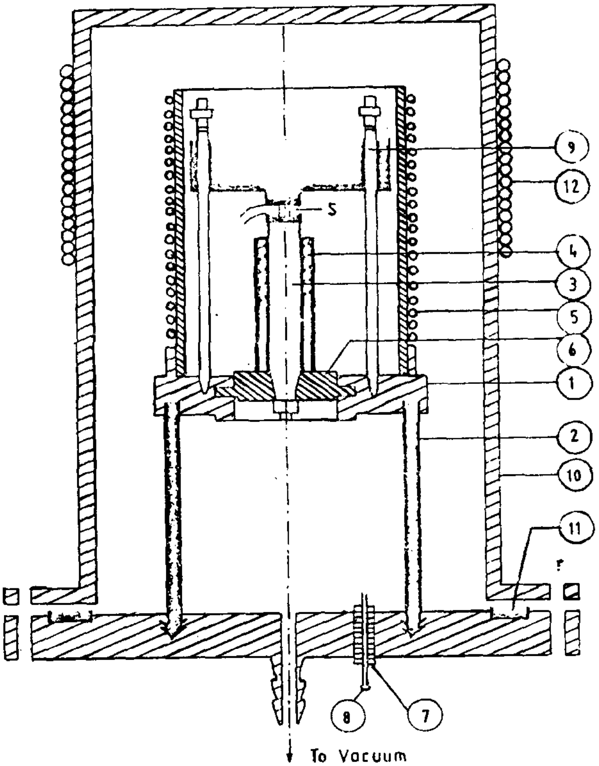

Fig. 1. Cross-section of the apparatus used for the measurements.

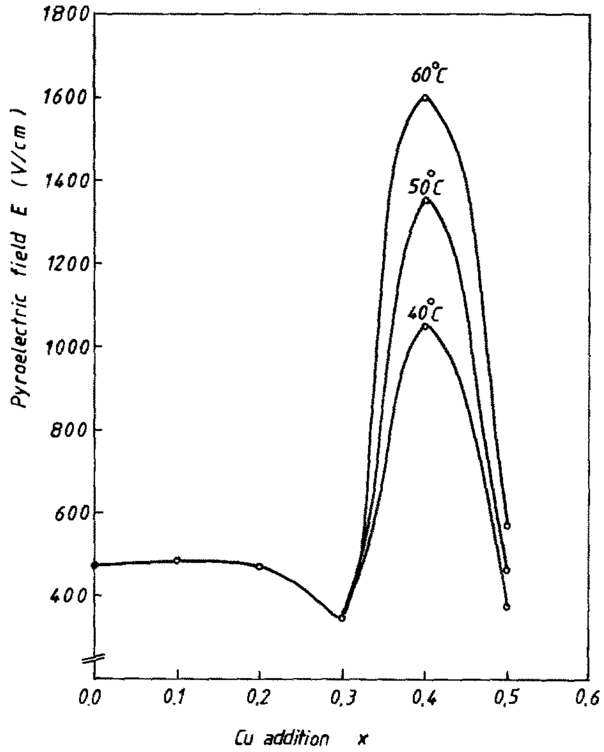

Fig. 2. Effect of Cu additions x on the pyroelectric field.

copper electrodes by means of pressure of the load (9) screwed to the rods. The base plate is surrounded by a metal jacket (10) which rests on an annular vacuum-tight rubber ring (11). A cooling copper coil (12) is sealed on to the surrounding of the metal jacket. For stability of measurements, the system is provided with an outlet for connection to a vacuum system (10^{-3} mm Hg).

For each sample the pyroelectric voltage was measured with the external heater only being used for uniformly heating the samples over the temperature range 20–250°C.

RESULTS AND DISCUSSION

Effect of Cu additions on the pyroelectric voltage of Ni–Zn ferrite

This effect is shown in Fig. 2 for temperatures of 40, 50 and 60°C. It was observed that the pyroelectric voltage decreased to attain a minimum value at $x = 0.3$, then increased sharply to attain a maximum value at $x = 0.4$. Previous measurements of the thermoelectric power of these compositions indicated that the conductivity was of p-type [14], and it has been suggested that the substitution of Cu^{2+} into $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}Fe_{2-x}O_4$ might cause the formation of excess vacancies. Also, lattice vacancies are created by substitution of impurities with anomalous valencies and by changes in stoichiometry [15]. Thus charged oxygen vacancies are introduced when Cu^{2+} replaces Fe^{3+}. These vacancies are believed to be sorbed at grain boundaries, retarding charge mobility and causing a decrease in the pyroelectric voltage with Cu additions to have a minimum at $x = 0.3$ at all temperatures. Besides, the vacancies introduced by doping are bound to the impurity ions and cannot move freely through the crystal to expedite mass transfer caused in low densification [16].

The maximum value of the pyroelectric voltage occurring at $x = 0.4$ may be due to the formation of excess vacancies, which would be oxygen vacancies, because Cu^{2+} ions have lower charge than Fe^{3+}, which may cause a high diffusion rate through the grain boundaries tending to increase the magnitude of the pyroelectric voltage.

Temperature dependence of pyroelectric coefficient for $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$

The pyroelectric coefficient was determined after measuring the pyroelectric voltage using the relations

$$i = \frac{\mathrm{d}Q}{\mathrm{d}t} = A\frac{\mathrm{d}P}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t} \tag{1}$$

$$\frac{V}{R} = A\frac{\mathrm{d}P}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t} \tag{2}$$

where i is the pyroelectric current, Q is the pyroelectric charge, A is the sample area, P is the polarization, V is the pyroelectric voltage and R is the sample resistance.

Dividing both sides of the last equation by the sample thickness d

$$\frac{V}{Rd} = \frac{A}{d}\frac{\mathrm{d}P}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t}$$

$$\frac{V}{d} = \frac{RA}{d}\frac{\mathrm{d}P}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t} \tag{3}$$

$$E = \rho\frac{\mathrm{d}P}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t} \tag{4}$$

$$E = \rho\gamma\frac{\mathrm{d}T}{\mathrm{d}t}$$

or

$$\gamma = \frac{E}{\rho\frac{\mathrm{d}T}{\mathrm{d}t}} \tag{5}$$

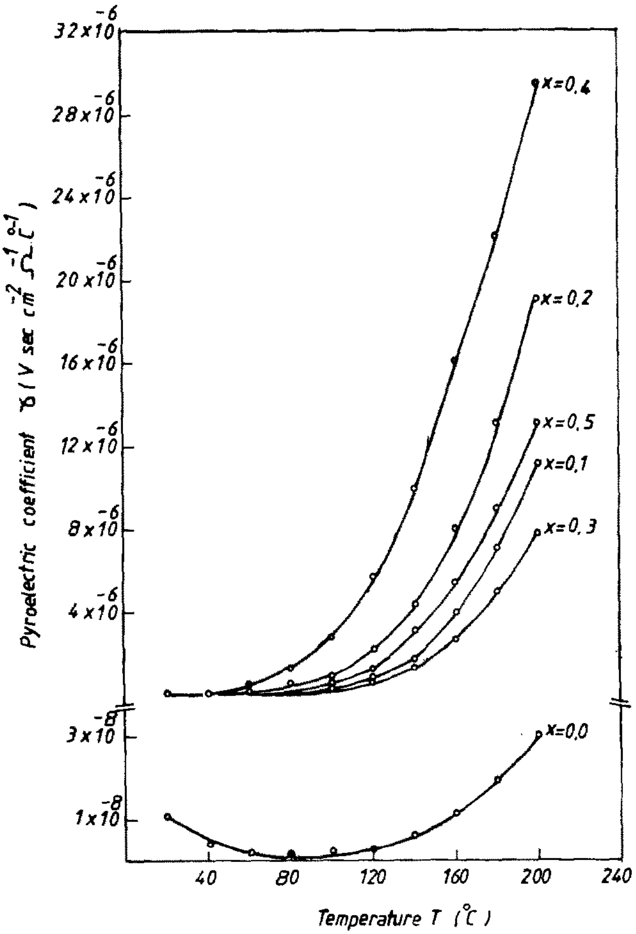

Fig. 3. Variation of the pyroelectric coefficient γ with temperature.

where γ is the pyroelectric coefficient, E is the pyroelectric field, ρ is the resistivity of the sample and $\mathrm{d}T/\mathrm{d}t$ is the rate of heating.

The pyroelectric coefficient was estimated using eqn. (5). For different compositions, it was noticed that the pyroelectric coefficient increased with temperature, as is clear from Fig. 3. In the case of ferrites, the mobilities of holes increase with increasing temperature [17–20]. In the equilibrium lattice there is little overlap between the wave functions of ions on the adjacent octahedral sites, with the result that holes are not free to move through a crystal but are fixed at the metal ions. In the presence of lattice vibrations, however, the ions occasionally come close enough together for transfer to occur with a high degree of probability. Thus, conduction is induced only by the lattice vibrations and consequently the carrier mobilities show an increase with increasing temperature, causing an increase of the electrical conductivity. The mechanism of dielectric polarization is

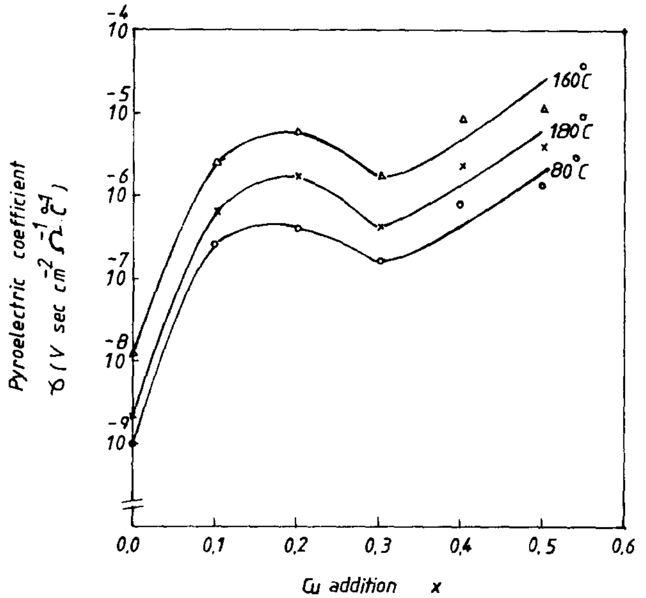

Fig. 4. Variation of the pyroelectric coefficient γ with Cu additions x.

similar to that of conduction [21]. The Cu^{2+} ions on the octahedral sites which take part in the hole exchange interaction are responsible for the polarization, giving rise to the pyroelectric coefficient γ.

In the light of such developments, it seems appropriate to investigate the electrical generation properties of a particularly attractive pyroelectric material.

Variation of pyroelectric coefficient γ with Cu additions x

Figure 4 shows the variation of the pyroelectric coefficient with Cu additions for $Ni_{0.65}Zn_{0.35}Fe_2O_4$ ferrite. The increase of γ with Cu additions up to $x < 0.3$ is due to the hole exchange between Cu^{2+} and Fe^{3+} ions at the octahedral sites. Moreover, the exchange of electrons between Fe^{2+} and Fe^{3+} ions at the B sites is the predominant process for n-type conduction. For compositions containing $x > 0.3$, hole conduction is the major process for p-type conduction. This process increases the polarization at the sample surfaces, giving rise to the pyroelectric coefficient. The number of Fe^{2+} ions at the octahedral sites plays a dominant role in the mechanism of conduction and dielectric polarization. This result is in agreement with the assumption of Reddy and Rao [22]. The increase of holes increases the generation of pyroelectric charges. The low value of the pyroelectric charges at $x = 0.3$ may be due to the reduction in the number of holes caused by the substitution of Cu^{2+} ions for Ni^{2+} ions with the same valency. For higher copper additions, Cu^{2+} ions substitute Fe^{3+} ions, creating holes because of the difference in valency, and this increases the polarization, causing an increase in the pyroelectric coefficient. The above results lead to the possibility of pyroelectric energy conversion using the ferrites.

Variation of the pyroelectric field with temperature T *and transition temperature* T_c*—relation between the pyroelectric field and* $1/T_c - T$

Figure 5 represents the temperature dependence of the pyroelectric field for the different Cu additions x. The results showed transition from the ferromagnetic to the paramagnetic state for all samples. The transition took place at a certain temperature T_c (corresponding to each composition) where the curve changes sign. The relation between the pyroelectric field and $1/T_c - T$ is represented in Fig. 6(a), (b) for all values of x in the

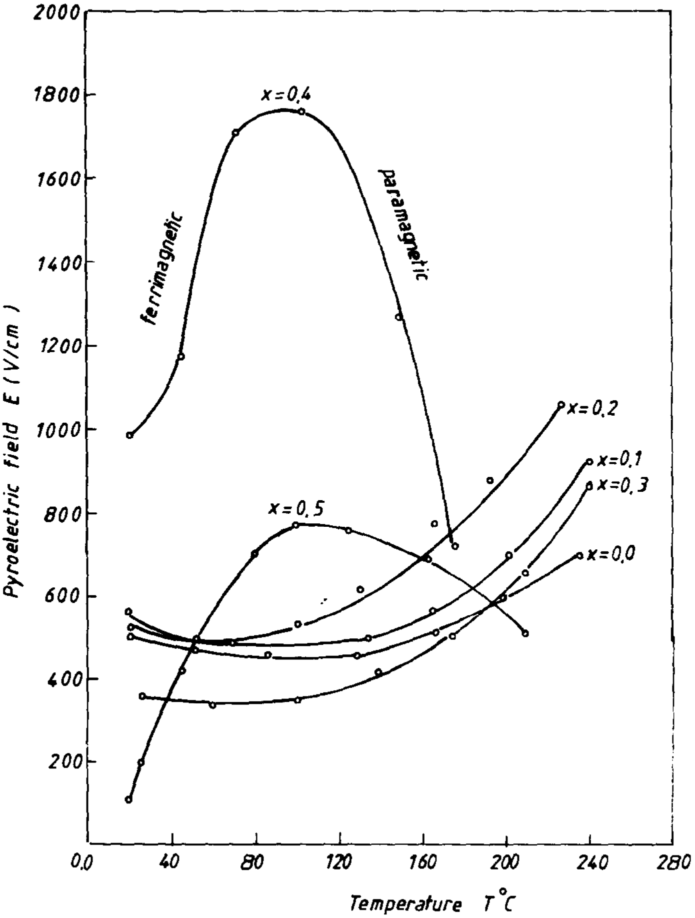

Fig. 5. Temperature dependence of the pyroelectric field for $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$.

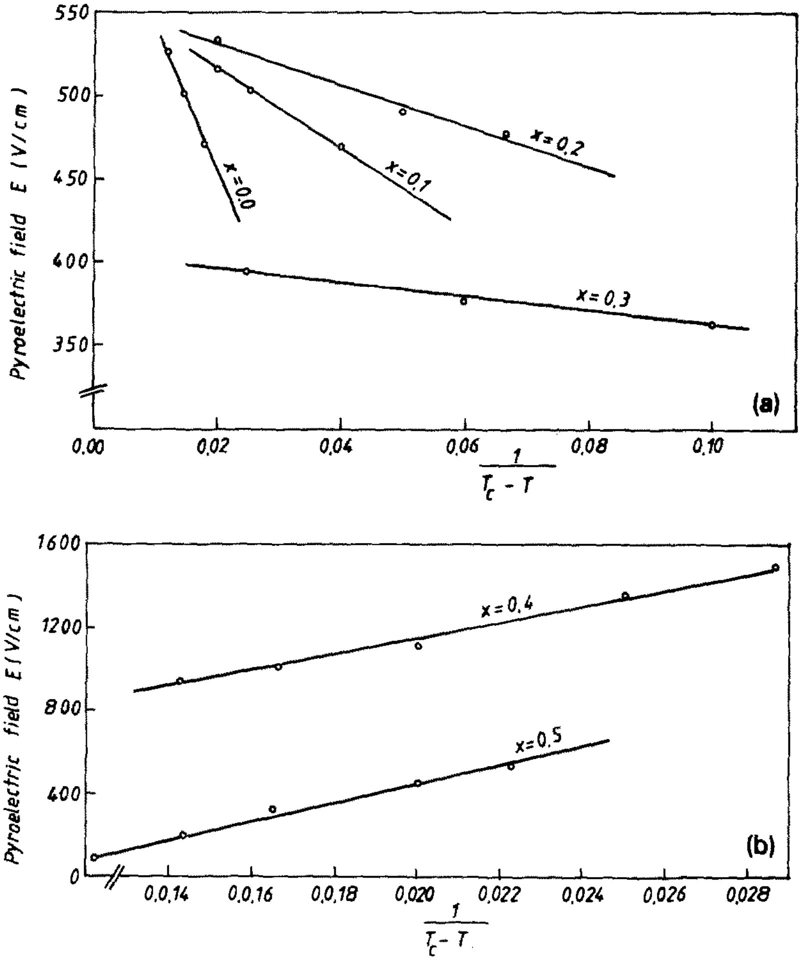

Fig. 6. Relation between the pyroelectric field and $1/(T_c - T)$.

ferromagnetic state. The obtained relation followed straight lines with negative slope for all $x \leq 0.3$ and positive slope for higher values of x. The decrease of the pyroelectric field with temperature, Fig. 5, may be due to the following. Since doping is a mechanism for introducing vacancies [15], an ion with the incorrect valency when it enters the lattice may form charged vacancies to maintain local electron neutrality. Thus, Cu^{2+} ions entering B lattice sites are assumed to create charged anion vacancies. The increase in temperature increases cation vacancies, which compensate some of the anion vacancies and cause the decrease of the pyroelectric field.

For $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ ferrites with $x > 0.3$, the increase of the pyroelectric field with temperature is due to the further generation of cation vacancies, which are the major in a p-type ferrite, resulting in local

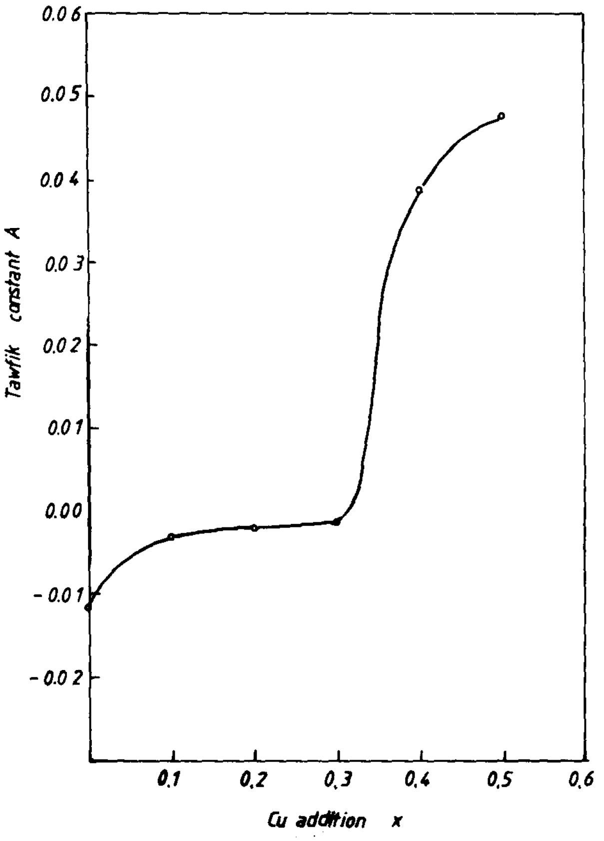

Fig. 7. Tawfik constant A versus Cu additions x for $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$.

displacements of holes in the direction of the electric field and then causing polarization. This explanation is similar to that of a previous discussion on Mn–Mg ferrites [22].

Tawfik constant A *as a function of Cu additions* x

The Tawfik constant A represents the slope of the straight line relating the pyroelectric field with $1/T_c - T$ in the ferromagnetic state of the ferrite. The values of A for all compositions are represented against x in Fig. 7. A has negative values for $x \leq 0.3$ because the majority of carriers are electrons. The hopping mechanism at B sites between Fe^{3+} and Fe^{2+} ions and between Cu^{2+} and Fe^{3+} ions causes generation of electrons. The positive value of A for $x > 0.3$ shows that the majority of carriers are holes. These holes increase with Cu additions because of the substitution of some Cu^{2+} ions instead of Ni^{2+} ions at the A sites, causing the latter to occupy the B sites. The difference in valency between Ni^{2+} and Fe^{3+} ions generates more holes, so increasing the constant A.

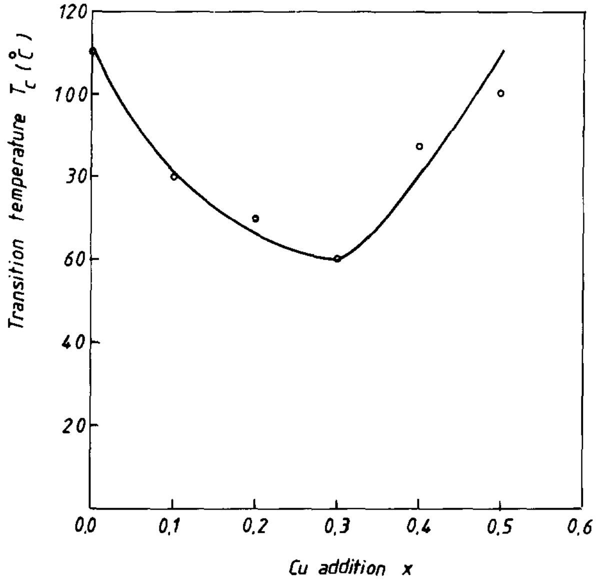

Fig. 8. Transition temperature dependence on $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ ferrite composition.

Transition temperature dependence on ferrite composition

Figure 8 represents the relation between Cu additions x and the transition temperature of $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ ferrites. The results show that the transition temperature T_c decreased with increasing x to attain a minimum value (60°C) at $x = 0.3$, then increased again for higher values of x. The decrease of T_c may be due to the substitution of Cu^{2+} ions for Fe^{3+} ions at the B sites, and the minimum value is attributed to the maximum replacement of Fe^{3+} ions by Cu^{2+} ions. For $x > 0.3$, some of the Cu^{2+} ions may replace the Ni^{2+} ions at A sites.

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