JOURNAL OF MATERIALS SCIENCE 29 (1994) 175–178

Electrical properties of Si^{4+} substituted copper ferrite

B. L. PATIL, S. R. SAWANT, S. A. PATIL, R. N. PATIL
Material Research Laboratory, Department of Physics, Shivaji University, Kolhapur 416004, India

The electrical resistivity, ρ, and Seebeck coefficient, α, for the system $Cu_{1+x}Si_xFe_{2-2x}O_4$ (where $x = 0.05$, 0.1, 0.15, 0.2 and 0.3) have been studied as a function of temperature. Temperature variation of the resistivity exhibits two breaks. Each break is associated with a change in activation energy. The conduction process at low temperature is governed by the reaction $Cu_A^{1+} + Cu_A^{2+} \rightarrow Cu_A^{2+} + Cu_A^{1+}$. However, at higher temperature, it is due to intersite cation exchange and reoxidation such as $Cu_A^{2+} + Fe_B^{3+} \rightarrow Cu_B^{2+} + Fe_A^{3+}$. Measurement of the Seebeck coefficient, α, from room temperature to 800 K reveals n-type conduction for the sample with $x = 0.05$, while the measurements for other samples show p-type conduction for lower temperatures and n-type conduction at higher temperatures. The activation energies in the paramagnetic region are found to be less than those in the ferrimagnetic region.

1. Introduction

Transport properties of ferrites are of great interest to many investigators [1–4]. Ferrites have semiconducting properties but the conduction mechanism is different and much less understood in comparison with the elemental group IV semiconductors, such as silicon and germanium. Verwey and Heilman [5] have described the conduction mechanisms to be due to the hopping effect which can be controlled by the addition of minor constituents. The present study is mainly concerned with the experimental results of electrical resistivity and Seebeck coefficient of copper ferrite with a small percentage of Si^{4+} as minor substitution. Abnormal thermal, magnetic and dielectric properties of copper ferrites have been reported by Rezlescu and Rezlescu [6]. The aim of the present work was to investigate the nature of the charge carriers and the possible conduction mechanism in Si^{4+}-substituted copper ferrite.

2. Experimental procedure

Samples of the system $Cu_{1+x}Si_xFe_{2-2x}O_4$ ($x = 0.05$, 0.1, 0.15, 0.2 and 0.3) were prepared by the usual ceramic technique. The pure oxides were mixed and then ground to very fine powder using an agate mortar. The samples in the form of discs were sintered at 1223 K for 20 h and slowly cooled to room temperature. The X-ray diffraction patterns were taken using FeK_α radiation. The d.c. resistivity of the samples was measured using the two-probe method with silver electrodes, and the temperature was measured using a chromel–alumel thermocouple. For thermoelectric power measurements, a temperature difference of 20 K was produced across the pellet with the help of a microfurnace fitted with the sample holder assembly.

3. Results and discussion

For all the samples, X-ray diffraction patterns show simple phase cubic spinel structure. Lattice constants for different compositions are given in Table I. The decrease of lattice constant with increase of Si^{4+} concentration can be understood in terms of the different ionic radii of the cations. In general, if the ionic radius of the substituted cation is smaller than that of the replaced cation, the lattice shrinks and this results in a decrease of the lattice constant. In the present case, Fe^{3+} ions (0.067 nm) are being replaced by the composite ion Cu^{2+}–Si^{4+} (0.069, 0.042 nm) in the formula unit. This may be the reason why lattice constant values in this system decrease.

The temperature dependence of the electrical resistivity, ρ, of the $Cu_{1+x}Si_xFe_{2-2x}O_4$ system is presented in Fig. 1. Plots of $\log \rho$ versus $1/T$ obey the Arrhenius relation $\rho = \rho_0 \exp \Delta E/kT$ for all samples. They are almost linear with two breaks giving three distinct regions. The activation energies in the paramagnetic region are less than those in the ferrimagnetic region ($\Delta E_3 < \Delta E_2$). The resistivity at a given temperature increases with the increasing Si^{4+} concentration.

Fig. 2 shows the temperature variation of the Seebeck coefficient, α, for all the samples; α is negative over the whole range of temperature for the composition with $x = 0.05$, indicating that it is n-type conductor. For the remaining samples, α is positive initially and after 430 K, it becomes negative. Cusp-like minima are observed near the Curie temperature for all samples. This indicates that the samples contain acceptor and donor centres with different relative predominance. Using the observed values of both ρ and α, the mobility, μd, is calculated as suggested by

0022–2461 © *1994 Chapman & Hall*

TABLE I Data on activation energies. ΔE. Transition temperatures and Curie temperatures for the $Cu_{1+x}Si_xFe_{2-2x}O_4$ system

Content, x	Lattice constant, a (nm ± 0.0002 nm)	Activation energy			Activation energy from mobility, E_2 (eV)	Transition temperature		Curie temperature, T_c (K)
		ΔE_1 (eV)	ΔE_2 (eV)	ΔE_3 (eV)		T_1 (K)	T_2 (K)	
0.05	0.8385	0.158	0.437	0.198	0.452	384	714	707
0.10	0.8344	0.198	0.477	0.278	0.473	400	689	667
0.15	0.8329	0.213	0.595	0.357	0.602	411	641	634
0.20	0.8299	0.238	0.675	0.437	0.682	416	625	603
0.30	0.8294	0.278	0.715	0.556	0.731	434	621	540

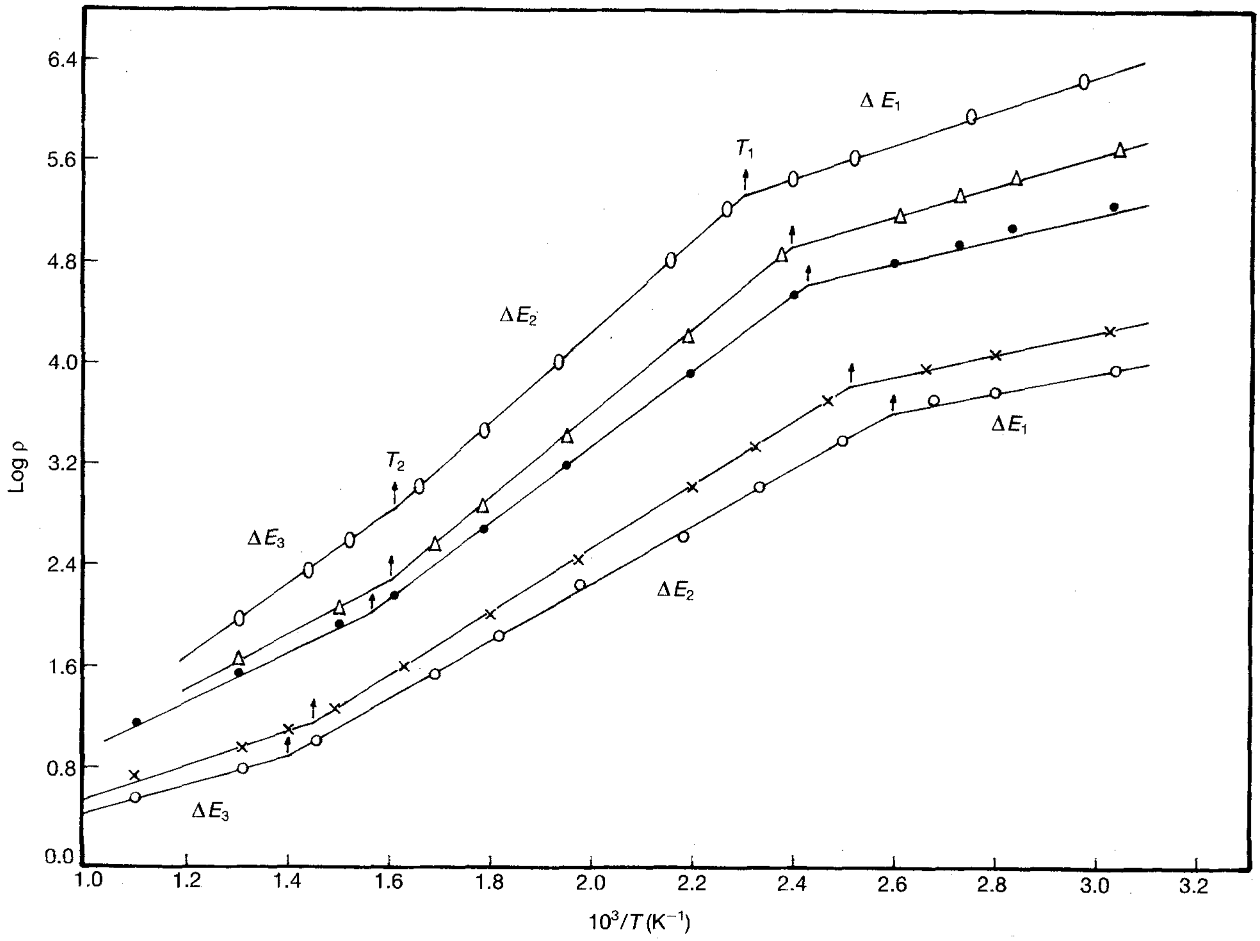

Figure 1 Temperature variation of resistivity for the system $Cu_{1+x}Si_xFe_{2-2x}O_4$ where x = (○) 0.05, (×) 0.1, (●) 0.15, (△) 0.2 and (0) 0.3.

Ghani *et al.* [7]

$$\mu d = \exp\left(\frac{\alpha}{2.3\ K/e}\right) \Big/ 2NO\rho e \qquad (1)$$

where NO is the concentration of Fe^{3+} ions on octahedral sites. The other notations have the usual meanings. The temperature variation of $\log \mu d$ is shown in Fig. 3. From these results, it is clear that μd increases exponentially with temperature according to $\mu d = \mu_0 \exp - \Delta E_\mu/kT$. Lattice constants, the activation energies, transition temperature and Curie temperatures are listed in Table I.

In general, the conductivity in ferrite has been associated with the presence of ions of a given element in more than one valence state. These ions become distributed over the crystallographically equivalent sites. The resistivity of the ferrites is controlled by the cation concentration on the B-sites. From the values of ΔE_1, which are in the range 0.15–0.27 eV, it appears that in the low-temperature range, the conduction is extrinsic. Similar results have been reported by Patil *et al.* [8]. The values of activation energies, ΔE_2, which are greater than 0.43 eV below the Curie temperature strongly predict that small polaron conduction dominates. Small polaron formation can take place in materials whose conduction electrons belong to incomplete inner d or f shells, which due to small electron overlap, tend to form extremely narrow bands [9]. The ions with $d^9(Cu^{2+})$ electronic configuration when situated at octahedral sites, cause a strong tetragonal distortion ($c/a > 1$). This distortion in the spinel structure affects the distance between the neighbouring Fe^{2+} and Fe^{3+} ions; as a result, the conduction process of the hopping electron is expected to be modulated.

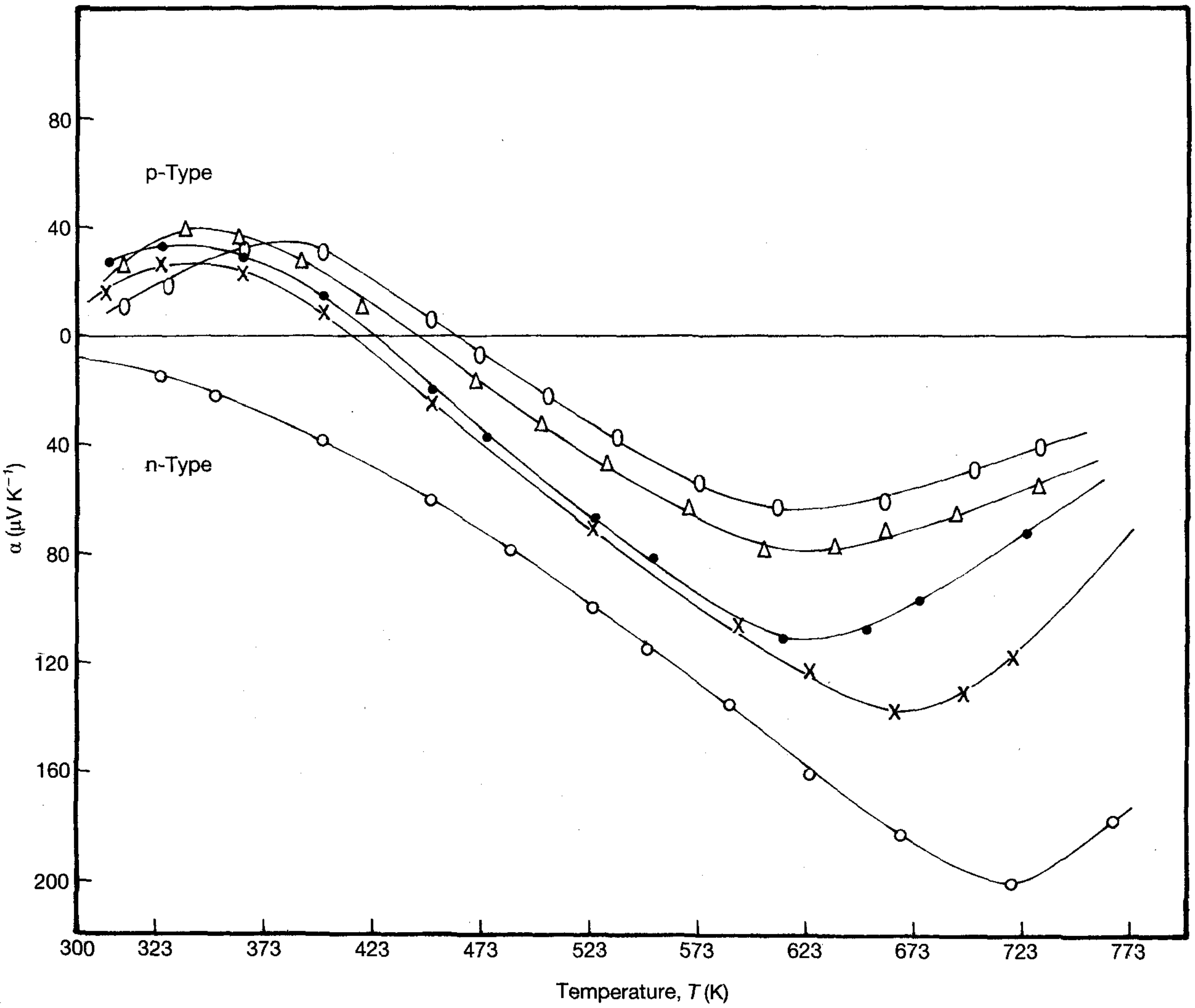

Figure 2 Temperature variation of thermoelectric power for the system $Cu_{1+x}Si_xFe_{2-2x}O_4$. For key, see Fig. 1.

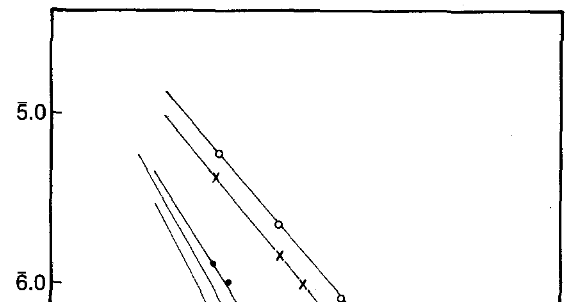

Figure 3 Temperature variation of mobility for the system $Cu_{1+x}Si_xFe_{2-2x}O_4$. For key, see Fig. 1.

The electrical properties of ferrites have been explained on the basis of tunnelling of electrons between Fe^{2+} and Fe^{3+} atoms on B-sites by Srinivasan and Srivastava [10]. It has been shown by Bates and Steggels [11] that the electrons which participate in the $Fe^{2+} \rightleftharpoons Fe^{3+} + e$ exchange process are strongly coupled to the lattice and tunnel from one site to the other due to a phonon-induced transfer mechanism. The activation energies calculated from mobility, E_μ, and from conductivity, i.e. ΔE_2, show good agreement. This clearly suggests that the conduction below the Curie temperature is mainly due to polaron hopping.

For all samples, it is observed that the activation energies calculated for the ferrimagnetic (ΔE_2) are higher than for the paramagnetic region (ΔE_3). Van Uitert [12] has shown that a very little deficiency or excess of iron ions changes the resistivity from a typically high value (10^{10} Ω cm) to a very low value (a few hundred ohm centimetres) in Ni–Zn ferrites. Bazynski [13] found that the magnetic ordering in Ni–Zn ferrite lowers the generation of carriers, whereas the mobility remains constant, so that the activation energy is higher in the ferrimagnetic region than in the paramagnetic region. Murthy *et al.* [14] confirmed this and suggested that the change in the slope can be either linked with magnetic ordering or with the conductivity mechanism. Hall effect and thermoelectric properties are widely used in the interpretation of the conduction mechanism in the semiconductors. In the case of low mobility materials such as ferrites, however, it is sometimes difficult to measure the Hall effect; in such cases, thermoelectric power (thermo e.m.f.) measurement is the only alternative. The sign of the thermo e.m.f. gives vital information about the type of conduction in ferrites. There are only two important conduction processes to be considered for $CuFe_2O_4$ at lower temperatures [15]. These are

$$\mathrm{Cu_A^{1+} + Cu_A^{2+} \longrightarrow Cu_A^{2+} + Cu_A^{1+}} \qquad (2)$$

$$\mathrm{Fe_B^{3+} + Cu_B^{2+} \longrightarrow Fe_B^{4+} + Cu_B^{1+}} \qquad (3)$$

The mixed valence small polaron Reaction 2 gives only p-type conduction depending on the relative concentration of Cu^{1+} and Cu^{2+} ions on A-sites. Seebeck coefficient data for all samples, except for $x = 0.05$ showed p-type conduction. Therefore, the predominant conduction may be due to Reaction 2. The formation of both types of centres (Cu^{1+}, Fe^{2+}) may result from the loss of oxygen during sintering [15]. In the present system, an increase of (Cu^{2+}, Si^{4+}) concentration with increase of x has the effect of reducing the net Fe^{3+} ion concentration by $(2 - 2x)$. This reduces the Fe^{3+}/Fe^{2+} ions available for conduction. Further localization due to Si^{4+} ions hinders the $Fe^{2+} \rightleftharpoons Fe^{3+}$ transition. Therefore, the conduction process due to Reaction 3 is less probable for the present system. When a metastable $CuFe_2O_4$ sample is heated, two temperature domains, $473\ K < 548\ K$ via intersite cation exchange and $573\ K < T < 673\ K$ via reoxidation, are noted, in which Cu^{2+} ions on B site increase. The intersite cation exchange is given as

$$\mathrm{Cu_A^{2+} + Fe_B^{3+} \longrightarrow Cu_B^{2+} + Fe_A^{3+}} \qquad (4)$$

Reaction 4 gives n-type conduction. Therefore, from the present study, the behaviour of α and ρ with temperature suggests that a mixed conduction process takes place because of simultaneous presence of acceptor and donor centres. Similar results have been obtained by Nanba and Kobayashi [16]. It is stated that Reaction 4 reduces Reaction 2, hence the change in the sign of the Seebeck coefficient is associated with intersite cation exchange. At higher temperatures, the predominant conduction process is due to Reaction 4. The observed cusp-like minima may be due to the filling of oxygen vacancies at that temperature which reduces the concentration of mobile electrons.

4. Conclusion

The following conclusions may be drawn.

1. The conduction process at low temperature is due to $\mathrm{Cu_A^{1+} + Cu_A^{2+} \rightarrow Cu_A^{2+} + Cu_A^{1+}}$, while at high temperature, it is due to Cu^{2+}/Fe^{3+} intersite exchange like $\mathrm{Cu_A^{2+} + Fe_A^{3+} \rightarrow Cu_B^{2+} + Fe_A^{3+}}$ and reoxidation of copper ions.
2. The change in the sign of Seebeck coefficient is associated with these reactions.
3. The conduction process above the Curie temperature is due to Cu^{2+}-rich and Cu^{2+}-poor domains.

Acknowledgement

One of the authors (BLP) thanks U.G.C. (New Delhi) for granting Teacher Fellowship for a PhD course.

References

1. A. I. EATAH, A. A. GHANI, M. F. EL-SHAHAT and E. J. EL-PASAMAWY, *Phys. Status Solidi* (*a*) **104** (1987).
2. E. W. GORTER, *Phillips Res. Rept.* **9** (1954) 302.
3. G. SRINIVASAN, *Phys. Status Solidi* **57** (1980) K 179.
4. A. J. BOSMANN and C. S. CREVE, *Phys. Rev.* **144** (1966) 763.
5. E. J. W. VERWEY and E. L. HEILMAN, *J. Chem. Phys.* **15** (1947) 174.
6. N. REZLESCU and E. REZLESCU, *Solid State Commun.* **14** (1974) 69.
7. A. A. GHANI, A. I. EATAH, M. F. EL-SHAHAT and E. J. EL-PASAMAWY, *Phys. Status Solidi* (*a*) **104** (1987) 793.
8. B. L. PATIL, S. R. SAWANT and S. A. PATIL, *ibid.* **132** (1992).
9. J. YAMASHITA and T. KUROSAWA, *J. Phys. Chem. Solids* **5** (1958) 34.
10. G. SRINIVASAN and C. M. SRIVASTAVA, *Phys. Status Solidi* **108** (1981) 665.
11. C. A. BATES and P. STEGGELS, *J. Phys. C* **8** (1975) 2283.
12. L. G. VAN UITERT, *J. Chem. Phys.* **23** (1956) 306.
13. T. BASZYNSKI, *Acta Phys. Polon.* **35** (1969) 631.
14. K. S. R. C. MURTHY, S. MAHANTY and J. GHOSE, *Mater. Res. Bull.* (*USA*) **22** (1987) 1665.
15. XIAO-XIA TANG, A. MANTHIRAM and J. B. GOODENOUGH, *J. Solid State Chem.* **79** (1989) 250.
16. N. NANBA and S. KOBAYASHI, *Jpn J. Appl. Phys.* **17** (1978) 1819.

Received 1 December 1992
and accepted 4 June 1993