

Note

THERMAL STUDIES ON THE ELECTRICAL CONDUCTION MECHANISM OF CuFe_2O_4

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(Received 5 January 1982)

Ferrimagnetic material technology has now reached a very advanced stage, so that the properties may be controlled to a large extent by the design engineer to suit the particular purpose of his device. The conduction mechanism in ferrite is described using both the band picture and hopping models. According to the band model, the temperature dependence of conductivity is mainly due to variation of charge carrier concentration with temperature, while in the hopping model the change of its mobility with temperature is considered to constitute the conduction current by jumping or hopping from one iron ion to the next.

Copper ferrite shows a remarkable variation in its magnetic properties depending critically on the thermal history [1,2]. This is attributed to the distribution of Cu^{2+} and Fe^{3+} among the two non-equivalent sites, tetrahedral (A) and octahedral (B), provided by the spinel structure. It is well known that slowly cooled copper ferrite has a tetragonal deformed spinel structure at room temperature. Snock [3] and Bertaut [4] reported that CuFe_2O_4 is cubic above 760°C , but Ohnishi and Miyahara [5] found, the temperature of transition from the tetragonal to the cubic structure to be 360°C . Rosenberg et al. [6] found that the transition from the tetragonal to the cubic phase for the slowly cooled composition is 175°C . Awad and Ahmed [7] also studied this transition and their results indicated a transition occurring at about 257°C . This transition phenomenon affects the magnetic thermal and electrical properties of CuFe_2O_4 .

Since the physical properties of any spinel depends not only on the kind of cation in the spinel but also on its distribution within the interstices, it is important to know the important effect on these physical properties. The aim of the present work is to investigate more extensively the electrical

properties of CuFe_2O_4 and study the effect of heat treatment on the transition point and d.c. resistivity.

EXPERIMENTAL

The measurements were carried out on polycrystalline samples. The samples were prepared by a standard ceramic technique from pure mixtures of the corresponding oxides. Ferric oxide and copper oxide were taken in calculated proportions and dry-ground into a fine powder which was well mixed using a ball-mill and then calcined at 750°C in air for 4 h soaking time. The calcined product was ground with a small quantity of butyl alcohol as binder material. The mixture was compressed to form pellets 12 mm in diameter and 2.5 mm thick. The sintering process was performed in air at 1100, 1150, and 1200°C for 5 h soaking time. Finally the samples were gradually cooled to room temperature at a rate of 1°C min^{-1} . This process was adapted to obtain the samples with a tetragonal structure. After sintering, the X-ray diffraction pattern was obtained for the sample in its powder form.

After firing, the samples were polished to obtain a circular disc with two uniform parallel surfaces. Indium amalgam was then put on the polished surfaces of the samples to form the electrodes.

The conductivity measurements were carried out, using the two-terminals d.c. method, over a wide temperature range from room temperature to 500°C . The electrical conductivity measurements were carried out under equilibrium conditions. The applied d.c. voltage was 1 V and was measured by an α -II digital multimeter. The temperature of the sample was measured using a calibrated iron-constantan thermocouple which was connected to a millivoltmeter of sensitivity 0.1 mV per one scale division.

RESULTS AND DISCUSSIONS

Since the ferrites are semiconductors, their conductivity (σ) should increase with increasing temperature according to the relation

$$\sigma = \sigma_0 \exp(-E_\sigma/KT)$$

Figure 1 shows the temperature dependence of d.c. conductivity. The values of activation energy (E_σ) are estimated using the above equation and are tabulated in Table 1.

From Table 1 it can be seen that the sintering temperature affects the conductivity process. The conductivity approaches minimum at 1150°C and consequently high activation energy. This may be due to the improved homogenization and structural perfection, as concluded by Van Uitert [8].

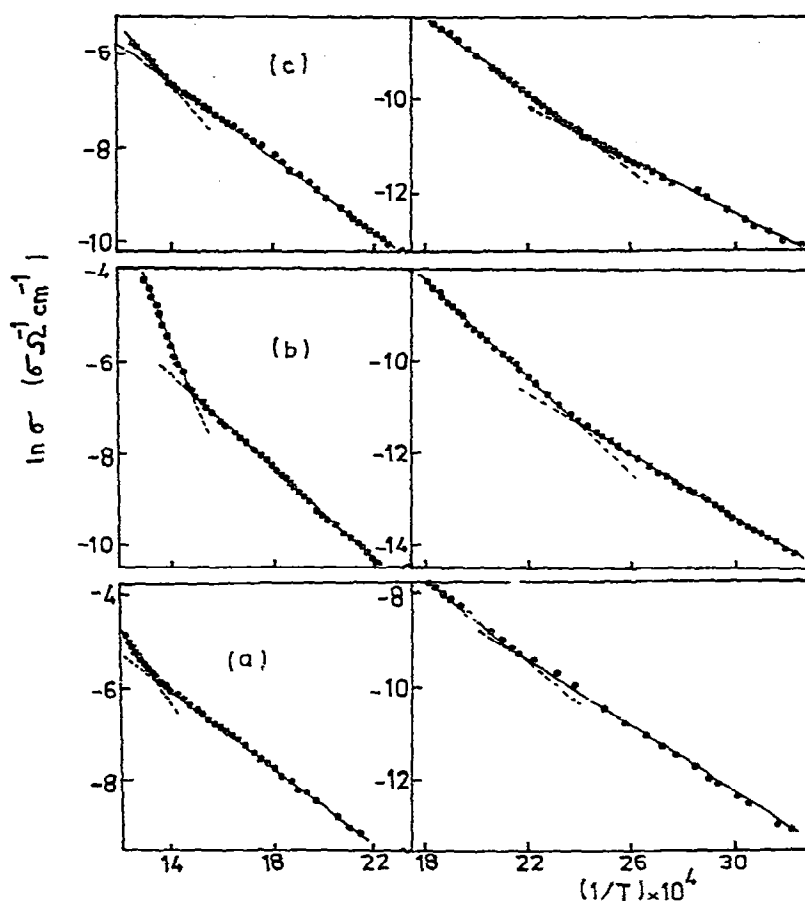


Fig. 1. Relation between $\ln \sigma$ and $10^4/T$ for CuFe_2O_4 at different sintering temperatures: (a) 1100°C ; (b) 1150°C ; (c) 1200°C .

The modification of the slopes in the $\ln \sigma$ vs. $1/T$ curve may be related to the phase transition from the tetragonal to the cubic phase in the first stage, which is in agreement with X-ray diffraction. The second stage is due to the magnetic ordering transition, i.e. passage from the ferrimagnetic to the paramagnetic region.

TABLE I

Sintering temp. ($^\circ\text{C}$)	$-\ln \sigma_{30^\circ\text{C}}$	Activation energy (eV)			Transition temp. from tetragonal to cubic, T (K)	Curie temp. T_c (K)
		E_1	E_2	E_3		
(a) 1100	13.40	0.32	0.37	0.72	449	746
(b) 1150	14.35	0.29	0.44	1.21	416	673
(c) 1200	13.30	0.26	0.36	0.51	417	714

The results obtained can be explained as follows. It has been shown [9] that the cation distribution of the copper ferrite is expressed by the formula



where the fraction x has been reported to have values in the range 0.1–0.14 for the tetragonal phase. The cation Cu^{2+} is known to form square bonds in complex ions, cupric oxide. Cations which form square covalent bonds can be accommodated in an octahedral site. Therefore Cu^{2+} cation is more stable in the B-site of the spinel lattice. The transition temperature (T) at which the phase change from tetragonal to cubic symmetry occurs varies with the magnitude of activation energy of the conduction mechanism. Where this occurs, there is a correlation between the lattice distortion and the activation energy [10] as measured by the temperature dependence of the conductivity. At high temperature some of the electrons are thermally excited from the covalent bond; when an electron is excited a hole is formed in the covalent bond, so that the coplanar covalent bonds in some octahedral sites (B-site) become partially ionic. Thus the loss of square bonds from the planes perpendicular to the c -axis is a cooperative phenomenon, and the transition from the tetragonal to the cubic phase occurs when the sample is heated. The conductivity behaviour on passing through the Curie point (T_c) may be explained qualitatively by assuming that the double exchange interaction takes place between Fe^{2+} and Fe^{3+} at the B-sublattice [11,12]. Thus we have encountered a relation between electrical conductivity and magnetism; namely, the lining up of the spins of adjacent incomplete d -shells of the metallic ions will be accompanied by an increase in the rate of migration of the charge carrier and hence by an increase in the electrical conductivity. However, the double exchange mechanism is accompanied by a slight increase in the activation energy in the paramagnetic region (above T_c), where short-range magnetic order usually persists.

CONCLUSION

The conductivity of CuFe_2O_4 can be changed by different sintering temperatures. The best sintering temperature for homogenization is 1150°C . The phase transition and Curie point also depend on the condition of preparation, such as heat treatment.

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