

Effect of Polymer Matrix on the Phase Transitions of CuFe_2O_4

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Received July 14 1998; in revised form December 2, 1998; accepted December 14, 1998

The effect of a polymer matrix on phase transitions in CuFe_2O_4 spinel oxide has been studied. XRD results show that cubic CuFe_2O_4 is obtained by quenching from 1173 K, while with CuFe_2O_4 -PEEK composite samples, the cubic form is obtained by quenching from considerably lower temperatures (~ 733 K). The change in resistivity with temperature of the quenched composite samples shows that the cubic samples quenched from < 1173 K undergo several phase changes during heating. Measurements of thermoelectric power indicate that the composite samples quenched from ≤ 1073 K show *n*-type conduction, and the sample quenched from 1173 K shows *p*-type conduction. © 1999 Academic Press

INTRODUCTION

CuFe_2O_4 is a tetragonally distorted spinel oxide with $c/a > 1$, and it undergoes tetragonal \rightarrow cubic phase transition at 633 K (1). Earlier studies of CuFe_2O_4 have shown that the cubic form cannot be obtained by quenching from temperatures < 1173 K (2, 4). Studies by Murthy *et al.* (2) have shown that metastable forms of CuFe_2O_4 are formed on quenching the ferrite from below 1173 K. On heating, the metastable state undergoes several phase changes. However, studies on CuFe_2O_4 -polymer composite samples show that cubic CuFe_2O_4 can be obtained when the composite is quenched from temperatures at low as 733 K (5). Thus, the present work was taken up to investigate the role of polymer matrix in the quenching process of CuFe_2O_4 composites.

EXPERIMENTAL

CuFe_2O_4 powdered samples were prepared by the method described elsewhere (2, 6). A series of composite samples with two different polymers, poly-arylether-etherketone (PEEK) and high-density polyethylene (HDPE), was prepared. The polymer content in the composite samples was varied. The two series of composite samples XPECF and XPKCF, where *X* is the weight percentage of polymer were prepared by mixing CuFe_2O_4 with the polymer. The

in the composite samples (*X* = 10, 15, 20, 25, and 33%), mixing was carried out by intensive grinding in an agate mortar. The solid solutions were then hot-pressed into pellets under a pressure of 5 tons/cm² at 383 K for XPECF and 623 K for XPKCF composite samples. Because the melting point and degradation temperature of PEEK is much higher than HDPE, the PEEK matrix was found to be suitable in studying the phase transition of CuFe_2O_4 . 15PKCF sample was chosen for the studies as the polymer crystallinity in this sample is not high, and the characteristics of the spinel oxide are easier to study (3). The quenched samples were prepared by heating the 15PKCF composite samples in air at different temperatures for 5 min in a classical furnace, and then they were quenched in liquid N₂. The code names and quenching temperatures are given in Table 1. X-ray diffraction analyses of the samples were carried out with a Philips X-ray diffraction unit (model PW 1710) using $\text{CoK}\alpha$ ($\lambda = 1.79 \text{ \AA}$) radiation with a Ni filter. The lattice parameter of the samples was calculated from the XRD patterns and is given in Table 1. Electrical resistivity measurements of the quenched samples were carried out on pellets of 10 mm diameter and 3 mm thickness prepared under a pressure of 5 tons/cm² between 300 and 745 K, in air, using the two-probe technique described elsewhere (2). The reduced thermoelectric power measurements between 300 and 745 K in air were carried out using a setup described elsewhere (7). The measurements were repeated and the results were found to be reproducible. The chemical stability of the composite samples with time was also established.

RESULTS AND DISCUSSION

Figure 1a shows the X-ray diffraction pattern of quenched (1173 K) CuFe_2O_4 and as expected it is single phase cubic CuFe_2O_4 . Figures 1b–1f show the X-ray diffraction patterns of copper ferrite composite samples (15PKCF) quenched from (b) 1173, (c) 953, (d) 853, (e) 733, and (f) 673 K respectively. The patterns show that all the samples except the sample quenched from 673 K are cubic. This is rather surprising as in all the earlier studies on CuFe_2O_4 it has

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TABLE 1
Sample Composition, Code Name, Quenching Temperature (T_q), Lattice Parameter (a_0), and Phase Transition Temperature of the Quenched Cubic Samples

Sample	Code	Quenching temperature (T_q)	Lattice parameter (a_0) ($\pm 0.0003 \text{ \AA}$)	Phase transition temperature (T_i)
CuFe_2O_4	CF	1173 K	8.382	603 K
15PKCF	CF1	1173 K	8.357	510 K
15PKCF	CF2	1073 K	8.357	560 K
15PKCF	CF3	953 K	8.383	568 K
15PKCF	CF4	853 K	8.379	574 K
15PKCF	CF5	783 K	8.377	565 K
15PKCF	CF6	733 K	8.385	598 K

been found that the cubic form of CuFe_2O_4 cannot be obtained by quenching from temperatures below 1073 K (1, 6). Figure 1e clearly shows that cubic CuFe_2O_4 is obtained when the polymer composite is quenched from a temperature

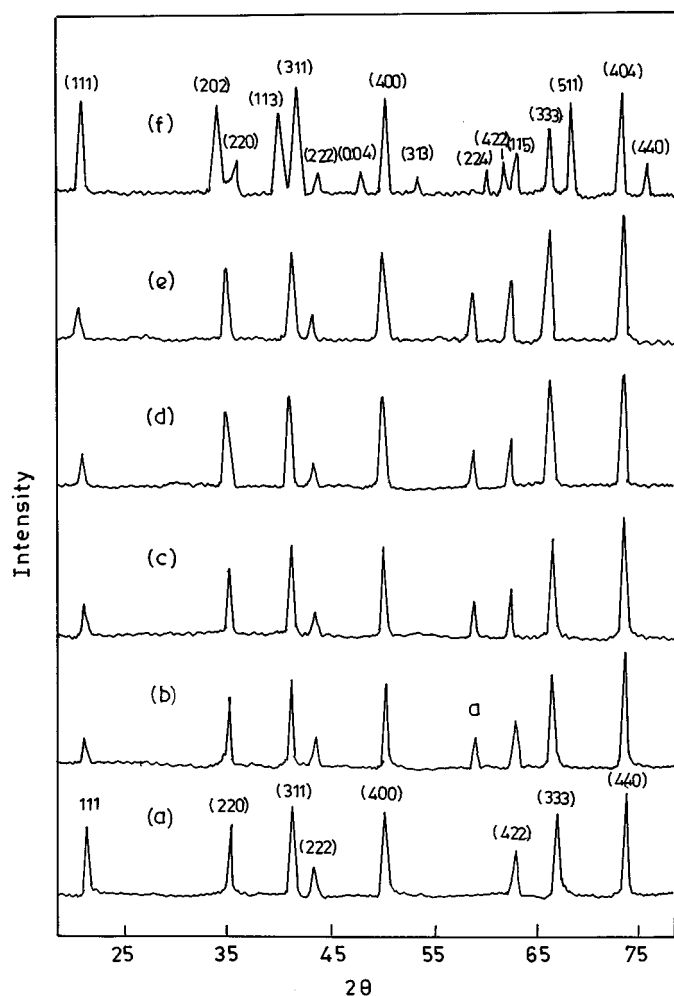


FIG. 1. XRD patterns of (a) quenched CuFe_2O_4 and composite samples quenched from (b) 1173 K, (c) 953 K, (d) 853 K, (e) 733 K, and (f) 673 K.

as low as 733 K. When the quenching temperature (T_q) is further lowered, i.e., 673 K, the cubic form is no longer obtained (Fig. 1f). Tang *et al.* (8) have extensively studied the thermal behavior of CuFe_2O_4 and have shown that a critical number of octahedral site Cu^{2+} ions per formula unit is necessary for cooperative distortion to tetrahedral symmetry at room temperature, and that a tendency of quenching-in of both $\text{Tet}_{\text{Cu}^{2+}}$ and oxygen vacancies on rapid cooling leads to the formation of cubic CuFe_2O_4 . The formation of cubic CuFe_2O_4 when the composite sample is quenched from below 1173 K suggests that in the presence of a polymer matrix, the quenching-in of the $\text{Tet}_{\text{Cu}^{2+}}$ of CuFe_2O_4 can be made effective at temperatures relatively lower than those in pure CuFe_2O_4 . Also, during high-temperature sintering prior to quenching, degradation of the polymer occurs, producing a reducing atmosphere that is likely to help in sustaining the oxygen vacancies, which may inhibit reoxidation required to introduce a reentrant tetragonal phase. The present results on CuFe_2O_4 -PEEK

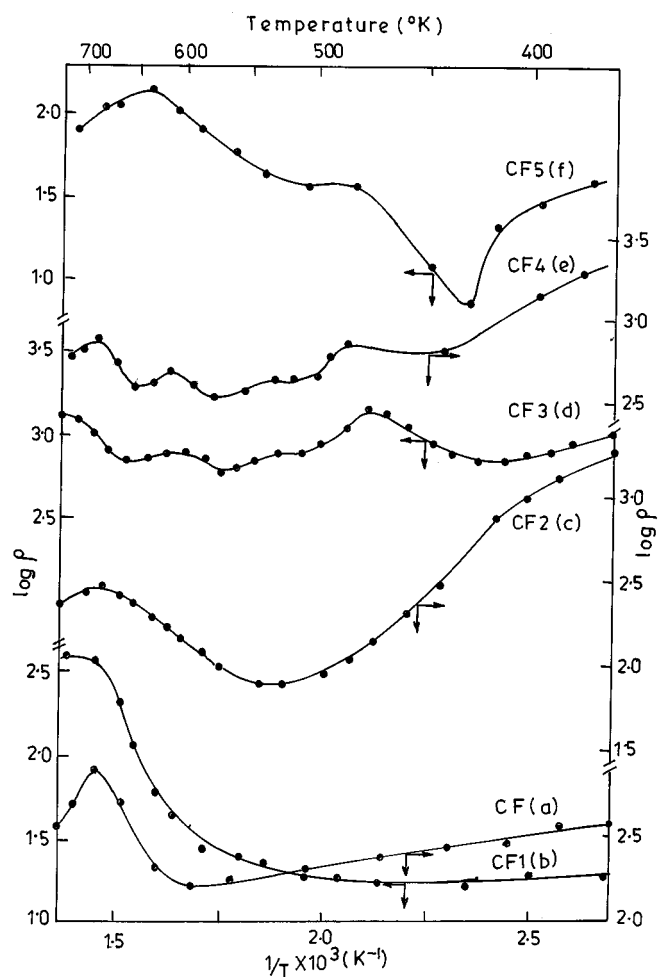


FIG. 2. $\log \rho$ vs $1/T$ heating plots for (a) CuFe_2O_4 quenched sample and CuFe_2O_4 composite samples quenched from (b) 1173 K, (c) 1073 K, (d) 953 K, (e) 853 K, and (f) 733 K.

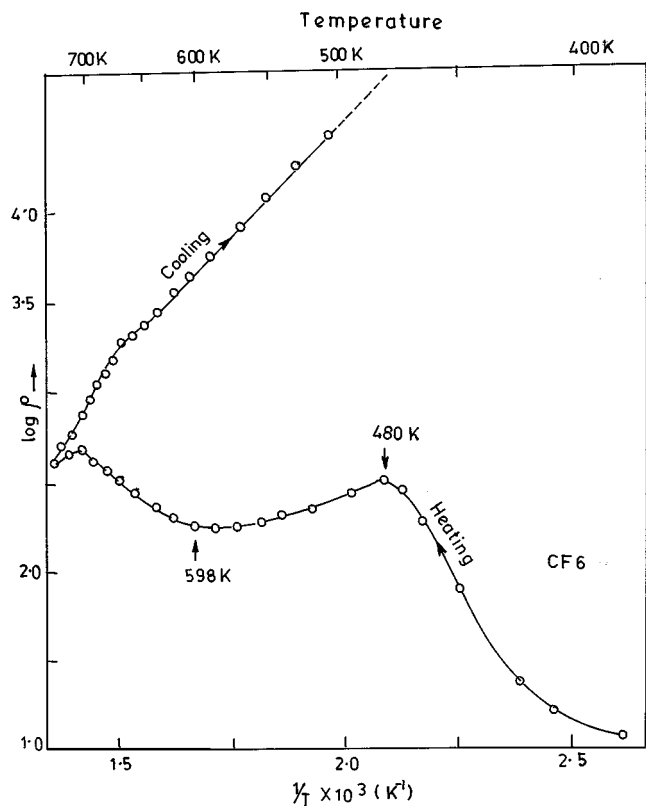


FIG. 3. $\log \rho$ vs $1/T$ heating and cooling plots for the CuFe_2O_4 composite sample quenched from 733 K.

compositions thus seem to be in accordance with the suggestions made by Tang *et al.* (8) in their studies on the phase transition of CuFe_2O_4 . The lattice parameter values of the cubic samples are given in Table 1. Table 1 shows that the lattice parameters of the quenched composite samples decrease gradually with increasing T_q and the value for CF6 (composite quenched from 1173 K) is almost equal to CF (CuFe_2O_4 quenched from 1173 K).

The $\log \rho$ vs $1/T$ heating plots of quenched CuFe_2O_4 (1173 K) and quenched 15PKCF samples, CF1, CF2, CF3, CF4 and CF5, are shown in Fig. 2. The heating and cooling plots of CF6 are shown in Fig. 3.

The heating curve of the quenched CuFe_2O_4 sample shows a linear $\log \rho$ vs $1/T$ plot up to 603 K. On further heating in air, nonlinearity sets in and the resistivity shows an increase with temperature in the temperature region 603–703 K followed by a sudden decrease on further heating (Fig. 2a). These results are similar to the results reported by Murthy *et al.* (2). The heating curve of CF1 is very similar to that of quenched CuFe_2O_4 and shows very little change in resistivity up to ~ 500 K (Fig. 2b), but above this temperature it increases up to 690 K and then almost becomes constant. The results of CF2 show a decrease in resistivity up to 560 K, then an increase between 560 and 680 K, followed by a sharp decrease above 680 K (Fig. 2c). The

heating curves of CF3 and CF4 (Figs. 2d and 2e) show multiple anomalies, and above 500 K these plots are similar to the reported $\log \rho$ vs $1/T$ plots of CuFe_2O_4 quenched from 953 and 853 K, respectively (2). Above 500 K the heating curves of CF5 (Fig. 2f) and CF6 (Fig. 3) appear to be similar to Fig. 2c, although below 500 K both samples show very irregular resistivity changes.

From these results it appears that on heating the composite samples show irregular changes in resistivity below 500 K. This is probably due to the presence of partially degraded polymer in the composite samples which further degrades on heating and affects the resistivity values of CuFe_2O_4 present in the composite samples. This view is supported by the absence of such irregularities in the resistivity changes of quenched CuFe_2O_4 , where the polymer matrix is absent, and CF1 and CF2 composite samples, where the polymer matrix has completely degraded during quenching. To confirm that the irregularities in the $\log \rho$ vs $1/T$ plots below 500 K are not due to any phase transition in cubic CuFe_2O_4 composites, the X-ray diffraction pattern of the quenched cubic sample ($T_q = 783$ K) after resistivity measurements up to 500 K was recorded. The X-ray pattern shows that the sample retains the cubic phase of CuFe_2O_4 up to 500 K (Fig. 3).

The change in resistivity with temperature of the quenched composite samples is irreversible as the $\log \rho$ vs $1/T$ heating plot is not retraceable during cooling (Fig. 4). Similar results have also been reported for quenched CuFe_2O_4 (2). From the $\log \rho$ vs $1/T$ heating plots of the quenched composite samples it is evident that the temperature region where there is an increase in resistivity due to phase transition shifts to lower temperatures with an increase of T_q (Table 1), implying that the phase transition temperature increases with decreasing quenching temperature of the composite. Such an observation was also reported by Onishi *et al.* (1) for pure CuFe_2O_4 . From Table 1 it is also evident that the phase transition temperature of CF6 is almost equal to CF. From the results of resistivity measurements it may be concluded that the multiple phase changes that are observed during heating CuFe_2O_4 quenched from various temperatures are also observed when composites of CuFe_2O_4 -PEEK samples quenched from various temperatures are heated.

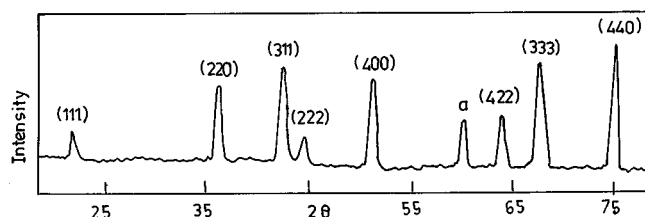


FIG. 4. XRD pattern of the composite sample quenched from 783 K after measuring the resistivity upto 500 K.

From thermoelectric power measurements of CuFe_2O_4 Tang *et al.* (8) have shown that quenched CuFe_2O_4 is *p*-type at room temperature and changes to *n*-type above 416 K. The results of TEP measurements on the quenched composite samples show that CF1 is *p*-type at room temperature and change to *n*-type above 408 K, but all the other composite samples are *n*-type at room temperature and in the studied temperature range CF2 and CF3 become *p*-type on heating. This could be due to degradation of the polymer matrix during quenching, which generates a reducing atmosphere that probably reduces the metal ions and helps in sustaining the oxygen vacancies. Studies by Parab (9) have also shown that in presence of a reducing atmosphere, the metal ion in CuFe_2O_4 is reducing leading to a cubic phase. The reduced metal ions may then act as electron donors, whereby the sample shows *n*-type conduction. This probably explains the *n*-type conduction shown by all the quenched composite samples (except CF1). The change from *n*-type to *p*-type may be due to oxidation of the metal ion during heating in air.

CONCLUSION

From these results it may be concluded that cubic CuFe_2O_4 can be obtained by quenching from temperatures ≥ 733 K, when a composite of CuFe_2O_4 in a polymer

matrix is quenched instead of pure CuFe_2O_4 . Similar to quenched CuFe_2O_4 , quenched CuFe_2O_4 composite samples also undergo multiple phase change during heating. However, unlike quenched CuFe_2O_4 , composite samples quenched from temperatures ≤ 1073 K show *n*-type conduction due to reduction of the metal ions during degradation of the polymer.

ACKNOWLEDGMENTS

The authors thank DST for financial support and Dr. A. Sen of D.M.S.R.D.E. Kanpur for supplying poly-aryl-ether-ether-ketone.

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