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Electrical Properties of the $CuCr_2O_4$ Spinel Catalyst

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Electrical resistivity of $CuCr_2O_4$ spinel obtained by a coprecipitation method was measured at various temperatures from 350 to 923 K in air. Oxidation of its surface chromium ions at various temperatures was determined by an iodometric method. The temperature dependence of resistivity and the presence of higher-valent chromium ions at higher temperatures indicated $CuCr_2O_4$ to be an extrinsic semiconductor. Log ρ vs $1/T$ plots yielded straight lines in the whole temperature range with two breaks, one around 550 K and the other around 730 K. The first break was attributed to the saturation of the surface with higher-valent chromium, while the second break was attributed to tetragonal-to-cubic phase transition in $CuCr_2O_4$. Log ρ vs $1/T$ plots obtained while cooling exhibited hysteresis near the second break, confirming this break to be due to a first-order diffusionless transition.

Introduction

$CuCr_2O_4$ has been well characterized as a tetragonally distorted normal spinel (*1*). Its thermal (*2–4*), magnetic (*5–8*), and optical (*9–11*) properties have been extensively studied. Thermal studies show that it undergoes a crystallographic phase transition from tetragonal to cubic at about 823 K. In other spinels, such phase transitions have been found to give rise to interesting electrical properties (*12–15*). The electrical studies reported on $CuCr_2O_4$ spinel so far have been limited to room-temperature measurements only. Measurement of electrical resistance (*16*), as well as KX-ray absorption spectroscopic studies (*17*) at room temperature, has shown this spinel to be an insulator. Theoretically, Goodenough (*18*) has also predicted $CuCr_2O_4$ to be an insulator on the basis of localized $3d$ electrons of Cr^{3+} ions.

The present investigation deals with measurement of electrical resistivity of $CuCr_2O_4$ spinel at higher temperatures and particularly near the phase transition temperature.

Experimental

Sample I: Copper chromite spinel was prepared by coprecipitation of the hydroxides of copper and chromium from the corresponding nitrate solutions, following the procedure of Yureva *et al.* (*19*), and subsequently heating at 873 K for 6 hr in air followed by slow cooling to room temperature.

Debye–Scherrer powder photographs of sample I were taken, using a Philips X-ray unit (Model PW 1012/10) and CrK_α (λ = 2.289 Å) radiation with vanadium filter. The lattice parameters were calculated using Hull's charts for tetragonal structures. Surface area of sample I was measured using a Carlo Erba Sorptometer (Model 1826) with

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nitrogen gas as adsorbate. The specific surface area was determined from the BET plots.

The extent of oxidation of surface Cr ions, at various temperatures, was determined by the following method: higher-valent surface Cr ions were first reduced to Cr^{3+} using 30% KI in concentrated hydrochloric acid. After removing all the KI and HCl with distilled water it was dried at 373K. Portions of this sample were heated in air at 473, 573, 673, 773, and 873K for 90 min and subsequently quenched to room temperature. The higher-valent "Cr" present on the surface of these samples was determined iodometrically (*20*).

Resistivity measurements on sample I were carried out after subjecting it to various pretreatments, described below.

Sample A: Prepared from sample I after reducing its higher-valent surface Cr ions to the Cr^{3+} state and subsequently pressing it into pellets of 10 mm diameter and 3 mm thickness, under a pressure of 10 tons/cm^2, using water as binder, which was later removed by keeping the pellets at 373K for some time.

Sample B: Prepared by annealing sample A at 773K for about 12 hr in argon atmosphere.

Sample C: Prepared by annealing sample A at 923K for 12 hr in air.

Measurements were also carried out on sample D, prepared by the solid-state reaction between cupric carbonate and chromic oxide. A high-temperature X-ray diffraction pattern of sample D was obtained at 923K (*21*).

Resistivity of these pellets was measured using a two-probe technique with an AEC megohmmeter (Model MOM2) in the high-resistance region and a Philips electro voltohmmeter (Model GM 6001) in the low-resistance region. Care was taken to minimize contact resistance. Temperature was recorded with a pyrometer using a Pt–Pt/Rh (10%) thermocouple. Prior to each measurement the sample was kept at the required temperature for half an hour.

Resistivity measurements on samples A, C, and D were done between 373 and 923K in air and on sample B between 300 and 673K in both argon and air.

Argon supplied by Indian Oxygen Ltd. was purified for oxygen, carbon dioxide, and water vapor by the usual methods.

Results

X-Ray powder diffraction photographs of sample I showed it to be a single-phase, tetragonally distorted, $CuCr_2O_4$ spinel having lattice parameters $a_0 = 8.53$ and $c_0 = 7.77$. Å. Its specific surface area was found to be 20.3 m^2/g.

Resistivities of all the samples studied followed the exponential law $\rho = \rho_0 \exp(q/kT)$ (ρ, the resistivity in ohm · cm, and T, the absolute temperature) in the respective temperature regions except at temperatures above 730K. Log ρ vs $1/T$ heating and cooling plots of sample A in air are shown in Fig. 1 (a and b, respectively). For sample B, corresponding plots up to 673K are shown in Fig. 2 (a and b). Figure 2 (curve c) also gives the plot in argon. Figure 3 shows the heating and cooling plots (a and b) for sample C in air between 373 and 923K, and the

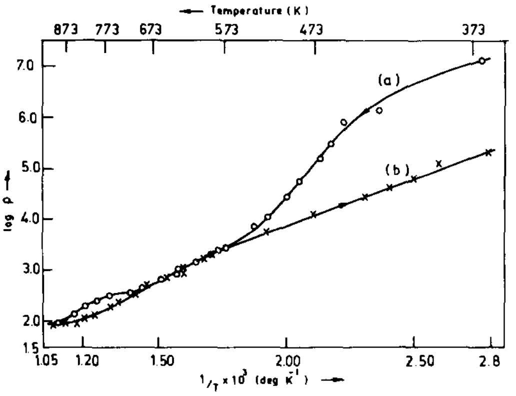

FIG. 1. Log-specific resistivity versus reciprocal of absolute temperature for sample A in air while heating (a) and cooling (b).

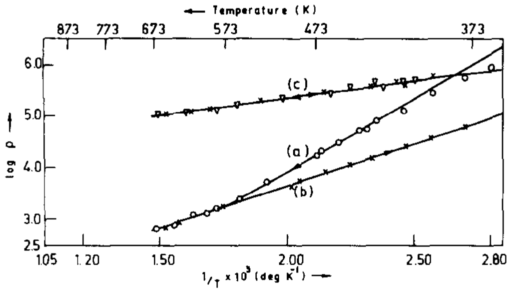

FIG. 2. Log-specific resistivity versus reciprocal of absolute temperature for sample B in air while heating (a), cooling (b), and in argon while heating and cooling (c).

corresponding plots for sample D are shown in Fig. 4 (a and b, respectively).

The curve (Fig. 1 (a)) for sample A shows a small deviation from linearity in the low-temperature region, and after that the resistivity falls rapidly with temperature up to 545 K. Then the rate of fall becomes small until at about 730 K, and from then onwards the plot deviates from linearity. Moreover, the heating plot is not retraceable while cooling between 923 and 730 K, as shown in Fig. 1 (b). Also, unlike the heating curve, the resistivity of the sample increases linearly without any break when cooled from 730 to 373 K. Furthermore, the room-temperature resistivity of the cooled sample is smaller than that of the starting material by about two orders of magnitude. Similar behavior is observed with sample B in the studied temperature region in air (Fig. 2 (a and b)).

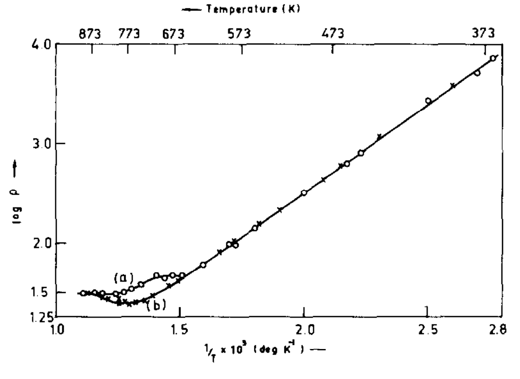

FIG. 3. Log-specific resistivity versus reciprocal of absolute temperature for sample C in air while heating (a) and cooling (b).

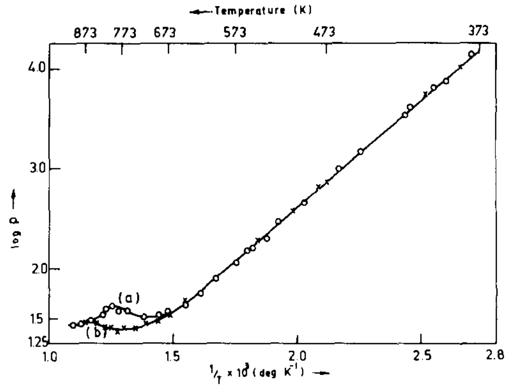

FIG. 4. Log-specific resistivity versus reciprocal of absolute temperature for sample D in air while heating (a) and cooling (b).

The change in resistivity of sample B in argon (Fig. 2(c)) is quite small and the rate of fall remains the same in the temperature region 300–673 K.

The plot obtained on heating sample C in air (Fig. 3(a)) is a single straight line without any breaks or deviations between 373 and 730 K. Also it is retraceable when the sample is cooled (Fig. 3(b)). However, above 730 K there is a gradual deviation from a straight line similar to in sample A, and on cooling below 870 K a hysteresis loop is obtained between 730 and 870 K. Similar behavior was observed for sample D, as shown in Fig. 4 (a and b). The high-temperature X-ray diffraction pattern of sample D, taken at 923 K, indicated that the phase present at this temperature was cubic $CuCr_2O_4$, lattice parameter $a_0 = 8.34$ Å.

The oxidation of surface Cr ions of the pure spinel at various temperatures is given in Table I.

Discussion

In $CuCr_2O_4$ all Cu^{2+} ions occupy tetrahedral sites while all Cr^{3+} ions occupy octahe-

TABLE I

OXIDATION OF SURFACE "Cr" IONS OF PURE $CuCr_2O_4$ CATALYST AT VARIOUS TEMPERATURES EXPRESSED IN mg ATOMS O UPTAKE/g CATALYST

Temperature	mg atoms O/g catalyst
373	0
473	0.62
573	1.231
673	1.26
773	1.30
873	1.24

dral sites. The Cu^{2+}–Cu^{2+} distance (≃3.57 Å) is comparatively larger than the Cr^{3+}–Cr^{3+} distance (≃2.92 Å) and theoretical calculations have shown that both the distances are larger than the critical cation distance R_c for d orbital overlap (*22*). Hence the outer d electrons of the metal ions in $CuCr_2O_4$ can be considered as localized and conduction may occur only by the hopping of electrons between metal ions in crystallographically equivalent sites. Since the Cu^{2+}–Cu^{2+} distance is comparatively large, the contribution from hopping among tetrahedral Cu^{2+} ions toward the total conductivity of the spinel is probably negligible. Thus conduction in stoichiometrically pure $CuCr_2O_4$ is likely to take place by hopping of electrons from lower-valent Cr^{2+} ions to higher-valent Cr^{3+} ions or from Cr^{3+} ions to Cr^{4+} ions, along the crystal lattice. However, for this, a Cr^{2+} or Cr^{4+} ion must be obtained by transferring an electron from a Cr^{3+} ion. Such transfers involve high activation energies which could possibly be made available at high temperatures. Hence under ordinary conditions it is highly improbable for stoichiometrically pure $CuCr_2O_4$ to have Cr^{2+} or Cr^{4+} species and thus it is expected to behave as an insulator. However, it has been conclusively established (*23–25*) that in air Cr^{3+} ions have a tendency to be oxidized to higher-valent states, particularly on the surface, and so in air, even at not too high temperatures, stoichiometrically pure $CuCr_2O_4$ cannot exist. This has also been established by iodometric analysis, which shows that annealing pure $CuCr_2O_4$ in air at 923 K results in approximately a 0.4% stoichiometric excess of oxygen (Table I). Since nonstoichiometry as small as 0.1% can give rise to extrinsic semiconduction (*26*), $CuCr_2O_4$ annealed in air may be classified as an extrinsic semiconductor. That the conduction is extrinsic in nature is also suggested by the small activation energies (0.56–0.35 eV) obtained from the resistivity measurements.

For an extrinsic semiconductor, the conductivity is expressed as $\sigma = ne\mu$ and its temperature dependence as $\sigma = \sigma_0 \exp(-q/kT)$, where n is the concentration of impurities or deviation from stoichiometry, e the electronic charge, μ the mobility of charge carrier, k the Boltzmann constant, and q the activation energy (*27*). From the above expression it is evident that for a semiconductor the conductivity will vary linearly with charge carrier concentration and exponentially with temperature. Such variations were observed for $CuCr_2O_4$ in the present investigation.

The presence of higher-valent Cr ions in $CuCr_2O_4$ has been reported to occur only on the surface (28–30). Recent X-ray photoelectron spectroscopic studies on a nonpromoted nonsupported copper chromite catalyst calcined at 513 K (*31*) have also shown the presence of Cr^{5+} species on the surface. Thus in Fig. 1 (a) the change in resistivity below 545 K may be attributed to the constantly increasing charge carrier concentration brought about by surface oxidation. The increase in charge carrier concentration at higher temperature is also apparent from the fact that the resistivity of the compound after cooling from 923 K to room temperature is smaller than that of the original compound.

Above 545 K, as indicated by the results of our iodometric analysis (Table I), surface oxidation is almost complete and so the fall in resistivity is small above this temperature, which is manifest as a break in the linear plot of log ρ vs $1/T$.

However, the decrease in resistivity below 545 K and the nonretraceability of the heating curve while cooling may also be due to annealing of grain boundaries during heating. To check this, sample B was prepared by prolonged annealing in argon at 773 K, thereby leaving no scope for further annealing of the grain boundaries during resistivity measurements. Figure 2 (a) shows that although the room-temperature resistivity of B is smaller than that of sample A, the general nature of the change is the same. Thus it appears that although there is some contribution to the resistivity from grain boundary annealing, the overall nature of the change in resistivity with temperature is not affected (Figs. 1(a), 2(a) and Figs. 1(b), 2(b)). Thus it may be concluded that the change in resistivity of sample A while heating in air between 373 and 573 K is unlikely to be due to annealing of grain boundaries. Furthermore, the resistivity plots of sample B in argon (Fig. 2 (c)) and sample C in air (Fig. 3 (a)) with no breaks in the vicinity of 545K give additional evidence to the fact that the above fall in resistivity is mainly due to oxidation of surface Cr^{3+} ions.

Though a small deviation from linearity in log ρ vs $1/T$ plots is observed at lower temperatures, i.e., 373–423 K, for both samples A and B (Figs. 1 (a) and 2 (a)), the other plots do not show any such deviation. The possibility of these deviations being due to any phase transition was ruled out as the thermal, magnetic, and crystallographic studies show no anomalies in this temperature region. Thus it seems that the deviation from straight line is not due to any phase transition, but is probably due to an irregular increase in the degree of surface oxidation during heating of samples A and B in the initial stages.

Above 730 K, as shown in Figs. 1, 3, and 4, the plot deviates from linearity up to 870 K, which may be due to the tetragonal-to-cubic phase transition of $CuCr_2O_4$. This was further confirmed by the high-temperature X-ray pattern of sample D, which showed the presence of cubic $CuCr_2O_4$ at 923 K.

The phase transition of $CuCr_2O_4$ has been studied by a number of workers (*3, 4, 32, 33*). Woztowicz (*33*) predicted the transition to be first order and the formation of the low-temperature tetragonal form of $CuCr_2O_4$ with $c/a < 1$ to be due to the alignment of compressed tetrahedra of oxide ions surrounding tetrahedral Cu^{2+} ions which is disturbed above the transition temperature, resulting in a cubic structure. Extensive X-ray studies have shown that at the transition temperature the cation distribution of the spinel remains unaltered and there is coexistence of both tetragonal and cubic phases over a certain temperature range (*2, 34*), which is characteristic of first-order transitions (*35*). Thus it appears that, in the present studies, the hysteresis loops observed in the resistivity curves (Figs. 1, 3, and 4) above 730 K are due to this first-order phase transition and the temperature range in which the two phases coexist are defined by the hysteresis loop.

From these results it may be concluded that the presence of higher-valent Cr ions as impurities are responsible for the extrinsic semiconductivity of $CuCr_2O_4$, and the first-order crystallographic phase transition from tetragonal to cubic is manifest in the hysteresis loop of the log ρ vs $1/T$ plot between 730 and 870 K.

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