JOURNAL OF MATERIALS SCIENCE 19 (1984) 3350–3354

Electrical transport in copper chromite catalyst

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The electrical conductivity, σ, and thermoelectric power, S, of copper chromite ($CuCr_2O_4$) are reported in the temperature range 295 to 815 K. A break (T_B) in the slope of the plot of $\log \sigma$ against T^{-1} was observed around 556 K. Apart from this break, the curves are linear, and their slopes correspond to activation energies of 0.60 eV ($T_B < 556$ K) and 1.22 eV ($T_B > 556$ K). A break (T_B') in the slope of the $-S$ against T^{-1} plot was also observed round 556 K. Apart from the break at this temperature, the S against T^{-1} curves are linear. At $T_B' > 556$, S can be expressed by the relation

$$S = -\left[\left(\frac{0.65\,\mathrm{eV}}{2eT}\right) + (0.42)\,\mathrm{mV\,K^{-1}}\right]$$

The mechanism involved in the electrical transport is the hopping of holes from Cr^{4+} centres to neighbouring Cr^{3+} ions. The typical hopping mobility of the holes is of the order of $10^6\,m^2\,V^{-1}\,sec^{-1}$. The mobility activation energy of the holes in $CuCr_2O_4$ decreases with temperature due to the smoothing of the potential barriers between Cr^{4+} and Cr^{3+} sites.

1. Introduction

It has been reported [1–8] that copper chromite enhances the decomposition and deflagration rate of ammonium perchlorate. The effect of copper chromite on the deflagration rate of propellants has also been reported in some earlier communications [9–12]. However, the chemistry of the copper chromite catalyst is unclear. Based upon chemical analysis it has been recently reported [13] that none of the commercial catalysts is copper chromite. For example, the empirical formula $9CuO{\cdot}Cr_2O_3$ or $8CuO{\cdot}CuCr_2O_4$ has been suggested for the Harshaw CuO 202 catalyst. Strahle and Handley [14] have reported that the Harshaw catalyst, CuO 202, is a mixture of approximately 82% CuO and 17% Cr_2O_3. It has been reported that copper chromite is formed during the calcination of mixtures of nitrates of copper and chromium at 900° C for 24 h [15], and mixtures of basic copper carbonate and chromium trioxide at 700° C for 2 h [16]. Very recently, calcined mixtures of basic copper carbonate and chromium carbonate have been found to be a more effective burning rate catalyst [17].

Among the physical properties of solid materials which have been used as heterogeneous catalysts in a variety of chemical industries, the electrical conductivity and thermoelectric power are of fundamental importance [18]. The electrical transport of catalysts is of basic importance in the determination of the relationship between electronic structures and catalytic properties of semiconductors. For the last few years, we have been trying to gain an understanding of the electrical transport and magnetic properties of transition and rare earth compounds [19–24]. This paper describes the electrical transport in $CuCr_2O_4$ in the temperature range 295 to 815 K. $CuC4_2O_4$ has a tetragonal lattice [25, 26] with $a = 0.6038$ nm and $c = 0.7787$ nm, and four molecules per unit cell.

2. Sample preparation and experimental technique

A mixture of basic copper carbonate and chrom-

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ium carbonate was prepared in the weight ratio of 1:2.37. The mixture was homogenized in an agate mortar using acetone and allowed to dry. The dried mass was heated for 2 h in a furnace which was maintained at 800° C and controlled to ± 10° C. Samples were taken out of the furnace two or three times during heating. These were crushed and homogenized with acetone and again calcined at the same temperature in order to ensure complete solid state reaction. This method of preparation of $CuCr_2O_4$ was the same as that reported earlier [27].

X-ray diffraction patterns of the reaction product were obtained with the help of the X-ray diffractometer using Cu*Kα* radiation at Bhabha Atomic Research Centre, Bombay (India). The product was found to be copper chromite since the *d* values in each case corresponded to those reported for copper chromite in the powder X-ray diffraction file. The electrical conductivity and thermoelectic power measurements were performed on pressed pellets using sample holder instruments and the procedure as described elsewhere [20, 23].

3. Results

Fig. 1 shows the current density–electric field (J–E) characteristics of a typical $CuCr_2O_4$ pellet using platinum foil as electrodes. It can be seen from this figure that the J–E curve is linear in an electric field from 2.5 to $20 \times 10^{-2}\,V\,m^{-1}$, indicating ohmic contact at the pellet–electrode interface. This was true throughout the temperature range measured. At very low fields and above a field of $20 \times 10^{-2}\,V\,m^{-1}$ the curves are not linear, and the contact is probably not ohmic. Therefore, we used the field which falls in the ohmic contact region. A similar type of behaviour was observed when the electric field was reversed.

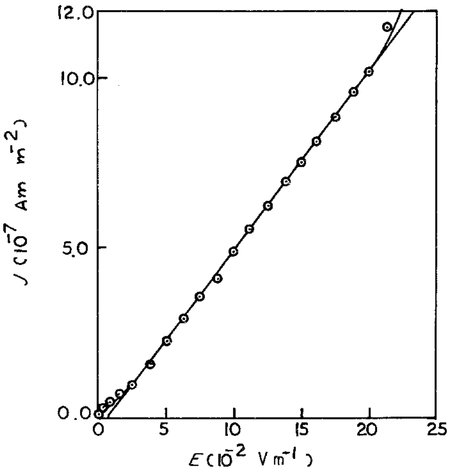

Figure 1 Plot of current density, J, against electric field, E, for $CuCr_2O_4$.

The electrical conductivity (σ_p) of the sintered pressed pellets does not depend upon the dimensions. However, the density (d_p) and σ_p depend upon P, but tend to be constant for pellets made at $P > 6.0 \times 10^8\,N\,m^{-1}$. The highest observed value of d_p ($3.66\,g\,cm^{-3}$) of the material, occurs simply because a sintered polycrystalline body is not truly solid, but contains many pores [28]. Therefore, a correction for the pore fraction, $f = (d_0 - d_p)/d_0$, 3.25×10^{-1} in our experiment, is made to obtain the crystalline value of the electrical conductivity (σ) according to the following relation [29]:

$$\sigma = \sigma_p \left(1 + \frac{f}{1 + f^{2/3}}\right) \tag{1}$$

The above relation holds when $f < 0.6$ [30]. S does not show any such pressure dependence, and probably needs no correction for pore fraction. The results for σ and S are shown in Figs. 2 and 3, respectively. It is observed from Figs. 2 and 3 that the plot of $\log \sigma$ against T^{-1} and of S against T^{-1} remain linear except for changes in slope around (T_B) and (T'_B), 556 K. In the two different temperature ranges, conductivities can be expressed by the following equations:

$$\sigma = 21.88 \times 10^2 \exp\left(\frac{-0.60}{2kT}\right)\ \Omega^{-1}\,m^{-1} \quad \text{for } T_B < 556\,K \tag{2}$$

and

$$\sigma = 11.15 \times 10^3 \exp\left(\frac{-1.22}{2kT}\right)\ \Omega^{-1}\,m^{-1} \quad \text{for } T_B > 556\,K \tag{3}$$

and the thermoelectric power by

$$S = -\left[\left(\frac{0.60\,eV}{2eT}\right) + (0.29\,mV\,K^{-1})\right] \quad \text{for } T'_B < 556\,K \tag{4}$$

and

$$S = -\left[\left(\frac{0.65\,eV}{2eT}\right) + (0.42\,mV\,K^{-1})\right] \quad \text{for } T'_B > 556\,K \tag{5}$$

The electrical conductivity, σ, at higher temperatures has been found to be independent of a.c. frequency ($f = 10^4\,Hz$) and time, indicating the absence of ionic conduction in this material.

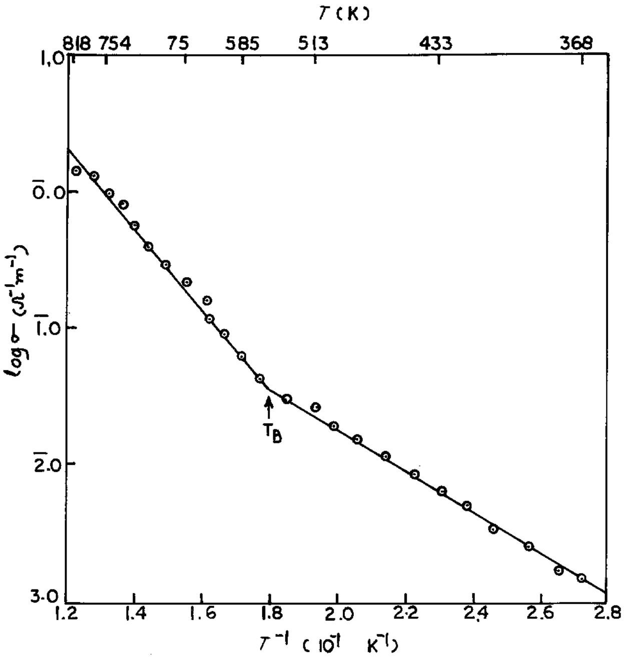

Figure 2 Variation of $\log \sigma$ ($\Omega^{-1}\,m^{-1}$) with inverse absolute temperature for $CuCr_2O_4$.

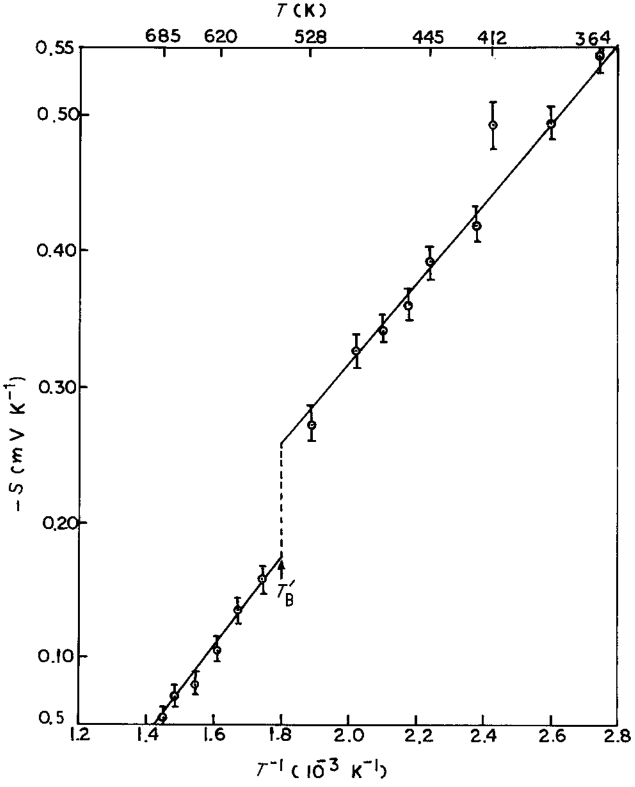

Figure 3 Variation of thermoelectric power, S ($mV\,K^{-1}$) with inverse absolute temperature for $CuCr_2O_4$.

4. Discussion

Copper chromite is a good semiconductor with a room-temperature conductivity of $0.82 \times 10^{-4}\,\Omega^{-1}\,\text{cm}^{-1}$. The thermoelectric power remains negative throughout the temperature range studied indicating that holes are the dominant charge carriers in this solid. It is usual to explain the electrical conduction in semiconductor solids using an energy band model. The relative position of these bands may not be depicted with certainty but copper bands may lie above the chromium band. The relevant bands for electrical conduction in this solid may be completely filled O^{2-}:2p bands, partially filled Cu^{2+}:3d and Cr^{3+}:3d bands and copper and chromium 4s bands. Both copper and chromium 3d bands will be split by a crystal field as well as due to correlation effects. The effect of this splitting will be that electrons in these bands will be almost localized and their band mobility will be extremely small: these bands will lie between the oxygen 2p and 4s bands of copper and chromium. Intrinsic electrical conduction can occur in this solid if (a) electrons are excited from oxygen 2p bands to split 3d bands of either chromium or copper; or (b) electrons are excited from oxygen 2p bands to 4s bands of either chromium or copper.

The second process may not be effective, because 4s bands are much above 3d bands. Hence the first process should be preferred on energy considerations. Also, owing to the wider nature of 4s bands in this process, electrons are expected to be dominant charge carriers, which has not been found experimentally true. Hence this process can be ignored. If the first process is to be dominant, the electrons excited to split 3d bands will be almost immobile and holes in oxygen 2p bands will dominate the conduction (Fig. 4). The electrical conduction in this substance will be given by the expression [31]:

$$\sigma = (2\pi k h^{-2})^{3/2} 2eT^{3/4} (me/m_{\text{h}})^{3/4} \left(1 + \frac{\mu_{\text{e}}}{\mu_{\text{h}}}\right) \times \exp\left(\frac{-E_{\text{a}}}{2kT}\right) \qquad (6)$$

or,

$$\sigma = \sigma_0(T) \exp\left(\frac{-E_{\text{a}}}{2kT}\right) \qquad (7)$$

where

$$\sigma_0 = (2\pi k h^{-2})^{3/3} 2eT^{3/4} (me/m_{\text{h}})^{3/4} \left(1 + \frac{\mu_{\text{e}}}{\mu_{\text{h}}}\right) \qquad (8)$$

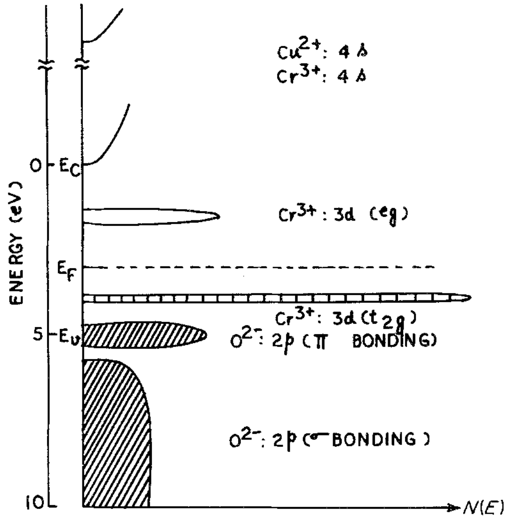

Figure 4 Schematic band diagram for $CuCr_2O_4$.

On a simple double band the temperature variation of thermoelectric power for this solid should be given by the relation

$$S = \frac{E_{\text{a}}}{2e}\left(\frac{C-1}{C+1}\right)\frac{1}{T} + \frac{2k}{e}\left(\frac{C-1}{C+1}\right) + \frac{3k}{4e}\log_{\text{e}}^{(a)} \qquad (9)$$

where $C = \mu_{\text{e}}/\mu_{\text{h}}$; the symbols used in the above equations have their usual meaning. The pre-exponential part of the equation has little temperature variation in comparison to the exponential part. Thus a plot of $\log \sigma$ against T^{-1} will yield a straight line with a slope corresponding to energy E_{a}. The plot (Fig. 2) has been found to be linear with a value of $E_{\text{a}} = 0.60$ eV for $T_{\text{B}} < 556$ K and $E_{\text{a}} = 1.22$ eV for $T_{\text{B}} > 556$ K. Similarly, the plot of S against T^{-1} will yield a straight line because mobility is almost constant over a small temperature interval, with the slope corresponding to the energy $[(C-1)/(C+1)](E_{\text{a}}/2)$. In view of the fact that the mobility of electrons in the 3d band is extremely small in comparison to the mobility of holes in oxygen 2p bands, C is very small and $[(C-1)/(C+1)] \sim 1$. The S against T^{-1} slope will correspond to energy $E_{\text{a}}/2$. This has been found experimentally to be true for $T < 556$ K (Fig. 3). However, it is not true for $T > 556$ K. This means some other mechanism begins to dominate electrical conduction above 556 K. Since there is essentially a very small change in the slope of the S–T^{-1} straight line, but S values fall around 556 K, this indicates an almost constant value of S with temperature, which in turn indicates that the charge carrier number is constant and they are not thermally generated. This points towards the existence of some sort of defect centre in these. Transition metals and their mixed oxides have a tendency to become oxygen deficient. Each oxygen vacancy may create two Cu^+ centres (it is much easier, energetically, to convert Cu^{2+} into Cu^+ in comparison with Cr^{3+} into Cr^{2+}). We believe that a large number of Cu^+ centres exists in this solid. The electrical conduction results due to jumping of electrons from Cu^+ defect centres to the Cu^{2+} normal sites. Thus, in addition to normal intrinsic band conduction, the conduction due to defect centres also contributes towards electrical conductivity. The former mechanism dominates below 556 K and the latter above it. The break temperature, $T_B = 556\,K$, shows a change in the type of conduction mechanism and has nothing to do with magnetic ordering and the phase transition temperature of the solid.

Acknowledgements

The authors are most grateful to Dr H. B. Lal, Department of Physics and Professor S. C. Tripathi, Department of Chemistry, Gorakhpur University, Gorakhpur for encouragement and taking a keen interest in the present work. Dr B. N. Tiwari and Dr C. S. Shukla wish to thank the Council of Scientific and Industrial Research, New Delhi for the appointment of a Scientist Pool.

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Received 17 May 1983
and accepted 16 January 1984