Electrical Conductivity & Thermoelectric Power of Copper(II) Chromite

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Electrical conductivity and thermoelectric power of copper(II) chromite has been measured. It is found to be a p-type semiconductor and appears to facilitate the electron transfer process in the combustion of ammonium perchlorate.

Single phased copper(II) chromite (CuCr₂O₄) has been prepared by two groups under different conditions using solid state reactions. Copper(II) chromite, prepared by calcining a 1:2 mole mixture of basic copper(II) carbonate [CuCO₃·Cu(OH)₂·H₂O] and chromium(III) carbonate [Cr₂(CO₃)₃] at 800°C for 2 hr, has been found to exhibit maximum efficiency as an ammonium perchlorate/polystyrene combustion catalyst. Therefore, it was proposed to study the electrical conductivity and thermoelectric power of copper(II) chromite sample showing maximum catalytic activity.

Copper(II) chromite prepared as described earlier, was characterised by chemical analysis (99% pure) and powder X-ray diffraction pattern. The crystal lattice belonged to body-centered tetragonal system with the lattice parameters, a = 6.04 Å and c = 7.78 Å. These values are in agreement with the reported ones. However, some workers have reported it to be face-centered tetragonal with a = 8.55 Å and c = 7.78 Å.

The assembly used in the measurement of direct current conductivity was similar to that used by earlier workers. The powdered sample was pelletized at 8354.22 kg cm⁻² so that it attained almost a constant density, smoothened on a thin emery paper and heated at 800±10°C for 2 hr. The thickness (0.240 cm) of the pellet was measured with the help of a screw gauge (0.001 cm) and area (0.9576 cm²) by a graph paper (cm). The pellet was gently silver painted and fixed in between the platinum electrodes fitted in the sample holder. The whole assembly was kept in the furnace near the Pt/Pl-Rh (13%) thermocouple. The voltage (dc for temperature) and current were recorded by a digital multimeter (Keithley type 171). The voltage (V) in stabilized power supply was also recorded. The value of σ was calculated using the expression σ = G·t·a, where G is conductance, t, the thickness and a is the area of the pellet. The experiments were carried out at different temperatures.

The assembly used in the measurement of thermoelectric power was similar to that used by earlier workers. The thermoelectric power was measured for thick pellet prepared at a pressure of 8633.71 kg cm⁻². The pellet was fixed in between the platinum electrodes fitted in the sample holder, the assembly kept in the furnace and the thermal gradient (ΔT) measured by a Pt/Pl-Rh (13%) thermocouple in terms of dc voltage. The ratio ΔE/ΔT gave the value of thermoelectric power, H. Experiments were performed at different temperatures.

The electrical conductivity (σ) and the thermoelectric power of copper chromite obey the following expressions:

\[ \sigma = 2 \left( \frac{2 \pi k T}{h^2} \right)^{3/2} (m_e m_h)^{3/4} e (\mu_e + \mu_h) \exp \left( \frac{-E_g}{2kT} \right) \]

or

\[ \sigma = \sigma_0(T) \exp \left( -\frac{E_g}{2kT} \right) \]  ... (1)

\[ H = \left( \frac{E_g}{2e} \right) + \frac{3k}{4e} \log \left( \frac{m_h}{m_e} \right) + \alpha \]  ... (2)

In the above equations, \( E_g \) is energy band gap of the solid, \( e \) is electronic charge, \( m_h \) and \( m_e \) are the effective masses and \( \mu_h \) and \( \mu_e \) are the mobilities of charge carriers (\( h \) for holes and \( e \) for electrons) in valence and conduction bands respectively. \( K \) and \( h \) are Boltzmann and Planck's constants respectively. \( \sigma_0(T) \) is a constant slightly dependent on temperature. Since in intrinsic semiconduction, the number of holes and electrons are equal and for large band gap, \( \mu_h \approx \mu_e \), the former should dominate in the conduction process. Therefore, the plot of \( \log \sigma \) versus \( 1/T \) is linear above 303 K as expected.

Since from Eq. (2) it is clear that \( m_h \) and \( m_e \) do not change with temperature, the plot of thermoelectric power \( (H) \) versus \( 1/T \) would be linear. It could be expected that at temperatures just above 303 K, \( \mu_h \) might be much higher than \( \mu_e \) contributing to \( \sigma \) as well as \( H \). As the temperature increases, the mobility of electrons in the conduction band also increases and starts contributing to \( H \). This movement of electrons reduces the value of \( H \) because both, the electrons and the holes, moving towards lower temperature end of the pellet, would neutralize the net thermoelectric voltage in order to have the lower energy. This is why,
H reduces with increase of temperature. It is also obvious from the plot of \( H \) versus \( 1/T \) that for \( T>303 \) K, \( H \) is positive showing that positive holes play a predominant role in the conduction mechanism. However, increase in mobility of electron with increase in temperature, needs an explanation since it is well known that mobility of a charge carrier may decrease or remain almost constant with temperature. The behaviour may be due to the formation of polarons. Being a p-type semiconductor, copper(II) chromite is expected to enhance the electron transfer process in the combustion of ammonium perchlorate/polypropellant and hence plays an active role of a catalyst.

References
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