

Electrical Studies on CuRh_2O_4

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Electrical resistivity of the CuRh_2O_4 spinel has been determined in air while heating and cooling between 300–923 K. The room temperature resistivity is of the order of 10 ohm cm and remains almost unchanged up to 563 K, above which it decreases rapidly with temperature. A break in the $\log \rho-1/T$ plot at 563 K is due to a change in the conduction process, and the phase change undergone by CuRh_2O_4 at 850 K is not manifest in the plot. © 1987 Academic Press, Inc.

Introduction

CuRh_2O_4 has a tetragonally distorted normal spinel structure at room temperature similar to that of CuCr_2O_4 (1), and both spinels undergo a tetragonal to cubic phase transition around 800–850 K (2). Studies on CuCr_2O_4 have established that it undergoes a first-order, diffusionless reversible phase transition (3). The studies on CuRh_2O_4 , particularly near its crystallographic phase transition, have been very limited and only magnetic properties have been studied by Blasse (2). Since electrical studies on CuCr_2O_4 gave a very clear picture of the nature of phase transition (3) similar studies on CuRh_2O_4 were performed to investigate the nature of its phase transition.

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Experimental

CuRh_2O_4 was prepared by impregnating stoichiometric amounts of Rh_2O_3 (Johnson and Mathey, Specpure) in cupric nitrate solution (BDH, Analar), which was then evaporated until dry and decomposed at 973 K. The pellets of the resulting oxides were fired at 1173 K in air for 48 hr, slowly cooled to 973 K, annealed for 24 hr, and subsequently cooled to room temperature. The annealing was to avoid the presence of $\text{Cu}_2\text{Rh}_2\text{O}_4$ in the final product.

A Debye-Scherrer powder photograph of the sample was obtained using a Philips X-ray diffraction camera (Model PW 1010) with a copper target and a nickel filter. Lattice parameters were determined using Hull's charts for tetragonal structures. Electrical resistivity measurements were

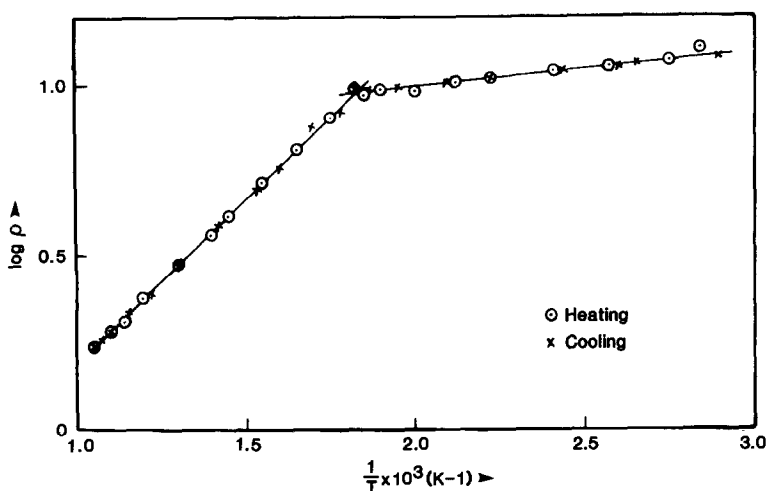


FIGURE 1

carried out by a method described in an earlier paper (3).

Results

The powder photograph of the sample showed that it was a single phase tetragonally distorted spinel with lattice parameters $a = 8.700 \pm 0.003 \text{ \AA}$, $c = 7.911 \pm 0.003 \text{ \AA}$ ($c/a = 0.912$), in agreement with published data. Figure 1 shows the logarithmic plot of electrical resistivity ($\log \rho$) versus the reciprocal of absolute temperature ($1/T$). The plot obtained is linear, with a change in slope at 563 K. The change in resistivity with temperature is small in the range 300 to 563 K and becomes significant above this temperature. The heating plot is retraceable while cooling over the whole temperature range.

Discussion

The results show that the resistivity change of CuRh_2O_4 is reversible in the studied temperature region. The linear plot shows a break at 563 K which is much below the tetragonal-cubic phase transition

temperature (850 K) of the spinel. Thus it appears that unlike in CuCr_2O_4 , the phase transition in CuRh_2O_4 has no effect on the electrical properties of CuRh_2O_4 . Also the nature of the $\log \rho - 1/T$ plot is different and the magnitude of the room temperature resistivity is almost five orders less than that of CuCr_2O_4 .

Figure 1 shows that below 563 K, the activation energy for conduction is 0.04 eV. This value, as well as the room temperature resistivity of CuRh_2O_4 , is almost the same as that reported for $\gamma\text{-Rh}_2\text{O}_3$ (4). From these similarities it may be suggested that up to 563 K conduction in CuRh_2O_4 is by octahedral rhodium ions and the conduction mechanism is probably the same as in $\gamma\text{-Rh}_2\text{O}_3$. The sudden fall in resistivity above this temperature probably implies a change in the conduction process. This change could be due either to the onset of pore conductivity at higher temperatures or to the electron hopping between widely separated (3.69 \AA) tetrahedral copper ions. The second probability seems more plausible as the high temperature activation energy of 0.18 eV is close to the value observed for CuO (0.2 eV), and also the

sudden fall in resistivity at higher temperatures is similar to that observed in CuO and CuAl_2O_4 (5). Hence, it may be suggested that the conduction process in CuRh_2O_4 below 563 K is by octahedral rhodium ions and that above this temperature is by tetrahedral copper ions. However, the possibility of pore conductivity at higher temperatures cannot be ruled out altogether.

In conclusion it may be said that although both CuCr_2O_4 and CuRh_2O_4 are normal spinels undergoing cooperative Jahn-Teller distortion around 800 K their electrical properties are dissimilar. While the electrical resistivity measurements on CuCr_2O_4 clearly show that it is a p -type semiconductor undergoing first-order, diffusionless reversible phase transition, the measurements on CuRh_2O_4 do not give any indication of its phase change. This is probably due to the difference in the character of $3d$ (Cr) and $4d$ (Rh) transition metal elements.

In $3d$ spinel oxides $R < R_c$ (R is the interatomic distance and R_c is the critical distance) and hence their electrical properties are likely to be sensitive to any change in interatomic distances that occur during phase transition. But when $R > R_c$, as in $4d$ spinel oxides, any change in R (up to $R = R_c$) due to phase transition is unlikely to affect the conduction process. Further work is in progress to study the conduction mechanism in $4d$ transition metal spinel oxides.

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