Thermoelectric Power Measurements of $CuCr_{2-x}Al_xO_4$ and $Cu_{1-x}Mg_xCr_2O_4$ Solid Solution Spinel Oxides

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Thermoelectric power of the solid solution system $CuCr_{2-x}Al_xO_4$ for $x = 0$–2 was determined between 300 and 673 K. $CuCr_2O_4$ shows p-type conduction and for $x > 0.08$ it changes to n-type. The results show that this is due to the presence of Cu_{tet}^{1+} ions produced during the redistribution of cations in the spinel lattice when aluminum is substituted for chromium ions. In the p-type samples charge hopping is between Cr_{oct}^{4+} and Cr_{oct}^{3+} and in the n-type, between Cu_{tet}^{2+} and Cu_{tet}^{1+}. The samples show n-type or p-type behavior depending on the dominant charge carrier present at a particular temperature. © 1989 Academic Press, Inc.

Introduction

$CuCr_2O_4$ is a tetragonally distorted normal spinel in which the distortion is due to the cooperative J–T effect caused by the Cu^{2+} ions present on the tetrahedral sites (*1–3*). De *et al.* have shown (*4*) that when chromium is replaced by aluminum the spinel becomes partially inverse and the distortion is absent for compositions $Al^{3+}/Cr^{3+} \geq 1$. When magnesium is substituted, the spinel remains normal and the distortion disappears for $Mg^{2+}/Cu^{2+} \geq 0.6$. Electrical resistivity measurements have shown that these oxides are semiconductors and the magnitude of resistivity is almost the same in all the aluminum-substituted tetragonal samples. Thermoelectric power measurements (TEP) at room temperature showed that introduction of aluminum changes the conduction type of the spinel;

i.e., $CuCr_2O_4$ is p-type but all the aluminum-substituted samples are n-type. The magnesium-substituted samples however remain p-type. The present work aims at studying the effect of aluminum substitution on the conduction type of the $CuCr_2O_4$ spinel.

Experimental

The solid solutions $CuCr_{2-x}Al_xO_4$ for $x = 0$, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.6, 0.8, 1.0, 1.2, and 1.6 (Table I) and $Cu_{1-x}Mg_xCr_2O_4$ for $x = 0.2$, 0.4, 0.6, 0.8, and 1.0 were prepared from stoichiometric mixtures of the respective nitrates by the method described in an earlier paper (*4*).

X-ray diffraction studies of all the samples were carried out using the Debye Scherrer powder technique with a Philips Model PW 1012/10 X-ray diffraction unit using a chromium target with vanadium filter for chromium-rich samples and a copper

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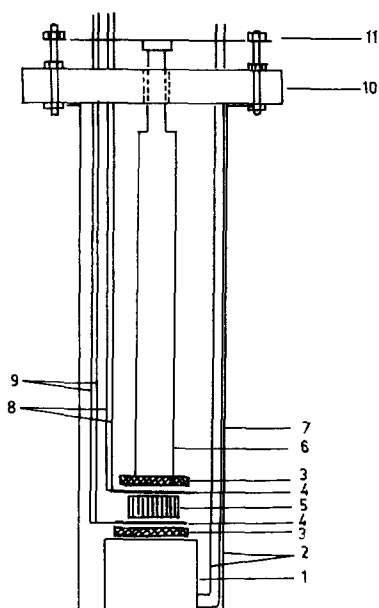* To whom correspondence should be addressed.

FIG. 1. Setup for thermoelectric power measurements. (1) Microheater, (2) microheater leads, (3) mica sheets, (4) platinum plate, (5) sample, (6) steel rod, (7) u-type steel frame, (8, 9) thermocouples, (10) sillimanite block, (11) screws.

target with nickel filter for copper-rich samples.

Conductivity measurements on all the samples were carried out in air between 300 and 873 K using a two-probe technique (5). Thermoelectric power measurements were also carried out in air from 300 to 673 K using the setup shown in Fig. 1. A temperature difference, ΔT, of approximately 25°C was maintained across the pellet. The temperature T, temperature gradient ΔT, and potential gradient ΔV developed across the pellet were recorded with a Philips Model PP 9004 microvoltmeter using a Pt–Pt/Rh (13%) thermocouple. The pellets were annealed at 923 K for 12 hr in air prior to the measurements.

ESCA measurements were carried out with ESCALAB MK II using a twin anode X-ray source composed of Mg and Al. The spectra were taken at 20°C and the spectrometer was evacuated to 10^{-9} Torr.

Results

X-ray diffraction patterns of $CuCr_{2-x}Al_xO_4$ show that at room temperature the samples with $x < 1$ are single-phase tetragonal spinels while those with $x > 1$ are single-phase cubic spinels. The patterns of $Cu_{1-x}Mg_xCr_2O_4$ show that the samples with $x < 0.6$ are single-phase tetragonal spinels while those with $x > 0.6$ are cubic spinels. Figure 2 shows that the plots of $\log \sigma T \rightarrow 1/T$ for all $CuCr_{2-x}Al_xO_4$ samples are linear. The thermoelectric power plots $(\alpha e/k \rightarrow 1/T)$ are shown in Figs. 3–6. Figure 3 shows that $CuCr_2O_4$ (NA0) is a p-type semiconductor with magnitude α increasing with temperature. The plots for NA1, NA2, and NA6 in Fig. 4 show that all the samples are
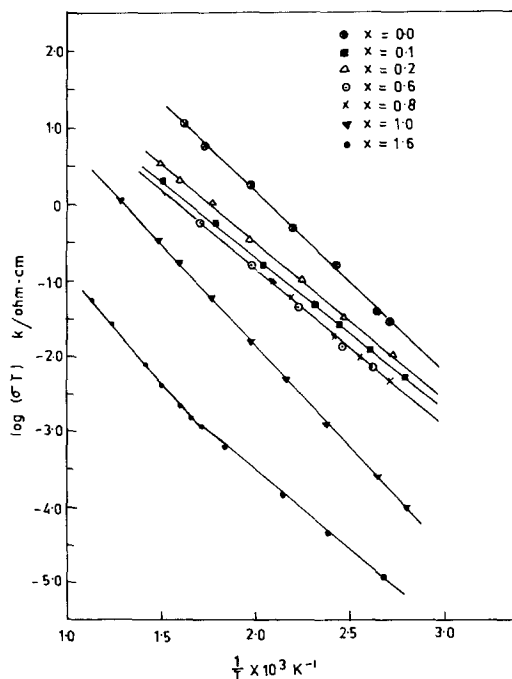

FIG. 2. Plot of $\log(\sigma T)$ vs reciprocal temperature for $CuCr_{2-x}Al_xO_4$.

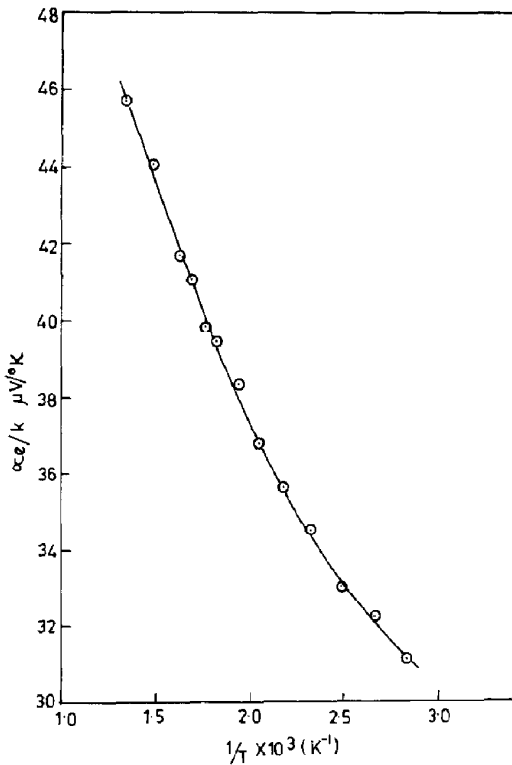FIG. 3. Plot of reduced thermoelectric power vs reciprocal temperature for NA0.

FIG. 4. Plot of reduced thermoelectric power vs reciprocal temperature for NA1, NA2, and NA6.

FIG. 5. Plot of reduced thermoelectric power vs reciprocal temperature for NA8 and NA10.

n-type with magnitude α increasing with temperature. For NA6, however, there is initially a slight decrease. Figure 5 shows the plots of NA8 and NA10 which are p-type with α decreasing with temperature. But above 400 K they become n-type and the temperature dependence is similar to that of NA1, NA2, and NA6. The plots of NA12 and NA16 in Fig. 6 again show the samples to be n-type in the temperature range studied and there is an initial decrease followed by an increase in the α value similar to that in NA6.

Table I gives the activation energies determined from the slopes of $\ln \rho$, $\ln(\rho/T)$, and $\alpha e/k$ vs T^{-1}, calculated values of activation energy due to the mobility E_μ, optical phonon frequency γ_0, and μ at 550 K for NA0, NA2, NA6, NA8, NA10, and NA16.
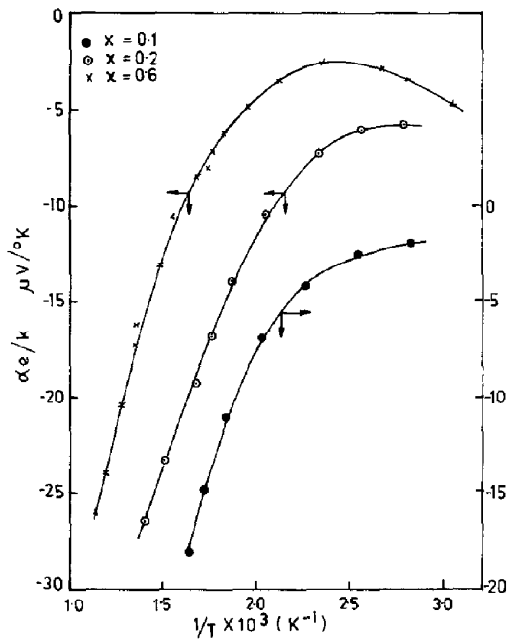
FIG. 6. Plot of reduced thermoelectric power vs reciprocal temperature for NA12 and NA16.
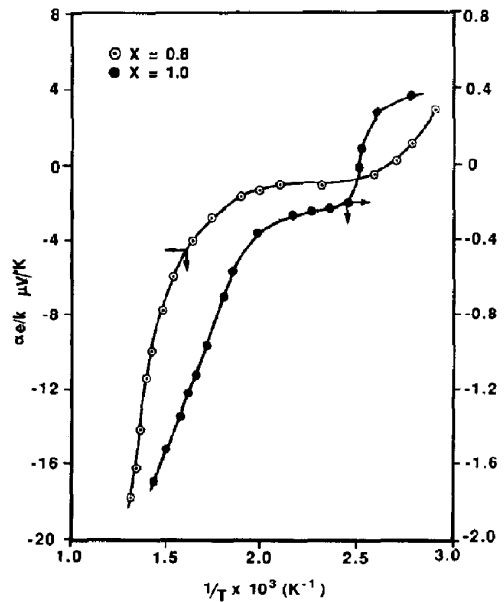
pletely in $CuCrAlO_4$. This was also evident from electrical conductivity measurements carried out by De *et al.* (*4*).

Figure 3 shows that in the temperature range studied NA0 is a *p*-type semiconductor; i.e., the conductivity can be represented as

$$\sigma = pe\mu,\qquad(1)$$

where *p* is the concentration of positive charge carriers, *e* is the absolute value of electronic charge, and μ is the drift mobility. The Seebeck coefficient α can be given as

$$\alpha = \frac{k}{e}\left[A + \ln\left(\frac{N_v}{p}\right)\right],\qquad(2)$$

where N_v is the effective density of states in the valence band, *A* is a constant depending on the dominant scattering mechanism, and *k* is Boltzmann's constant.

The ratio N_v/p can be determined by the positon of the Fermi level (E_F) with respect to the top of the valence band,

$$p = N_v \exp(-E_F/kT).$$

Generally for a semiconductor α decreases as the temperature is raised, but Fig. 3 shows that $\alpha e/k$ increases with temperature. Such an increase has also been observed in other semiconducting materials, viz., boron carbide, $Y_{1-x}M_xCrO_3$, and

Discussion

Structural and thermal studies on aluminum-substituted $CuCr_2O_4$ have shown that the tetragonal distortion is reduced when Al^{3+} is substituted for Cr^{3+} due to distribution of copper on both sites of the spinel lattice and the distortion disappears com-

TABLE I

ACTIVATION ENERGIES DETERMINED FROM THE SLOPES OF $\ln p$, $\ln(p/T)$ AND $\alpha e/k$ VS T^{-1a}

Sample	Code	Activation energies (eV)			E_μ(eV)	γ_0(sec^{-1})	$\mu_{550\,K}$ (cm^2 V^{-1} sec^{-1})
		$E(p)$	$E(p/T)$	$E(\alpha e/k)$			
$CuCr_2O_4$	NA0	0.35	0.374	1.29 $\times$ 10^{-3}	0.372	5.071 $\times$ 10^{11}	3.54 $\times$ 10^{-6}
$CuCr_{1.8}Al_{0.2}O_4$	NA2	0.395	0.434	1.54 $\times$ 10^{-3}	0.432	6.858 $\times$ 10^{10}	2.01 $\times$ 10^{-7}
$CuCr_{1.4}Al_{0.6}O_4$	NA6	0.395	0.434	1.64 $\times$ 10^{-3}	0.432	5.974 $\times$ 10^{10}	1.728 $\times$ 10^{-7}
$CuCr_{1.2}Al_{0.8}O_4$	NA8	0.410	0.452	7.92 $\times$ 10^{-4}	0.451	2.972 $\times$ 10^{10}	5.716 $\times$ 10^{-8}
$CuCr_{1.0}Al_{1.0}O_4$	NA10	0.510	0.552	2.236 $\times$ 10^{-4}	0.552	6.868 $\times$ 10^{10}	1.576 $\times$ 10^{-8}
$CuCr_{0.4}Al_{1.6}O_4$	NA16	0.380	0.422	7.031 $\times$ 10^{-4}	0.421	3.956 $\times$ 10^7	1.418 $\times$ 10^{-10}

a Calculated activation energy due to mobility E_μ, optical phonon frequency γ_0, and mobility μ at 550 K.

some manganites and garnets (6–9). Stoichiometrically pure $CuCr_2O_4$ is expected to behave as an insulator but the presence of excess oxygen (0.4%) produced during annealing of the sample in air at 923 K makes this spinel a p-type extrinsic semiconductor where the conduction occurs by charge hopping between Cr_{oct}^{3+} and Cr_{oct}^{4+} ions (5). Hopping conduction in $CuCr_2O_4$ is evident from the linear nature of the plots of log $(\sigma T) \rightarrow 1/T$. Also, the γ_0 values calculated from the intercept of the ln $\rho/T \rightarrow 1/T$ plot are similar to those of Metselaar et al. (10) using the equation

$$\ln(\rho/T) = -\ln(N_v e^2 d^2 \gamma_0/k) + (E_F + E_\mu)/kT, \quad (3)$$

where d is the jump distance, γ_0 is the optical phonon frequency, and E_μ is the activation energy of mobility. That these values were found to be in the range expected for optical phonons further supports the phonon-aided conduction mechanism. The values of E_μ (Table I) determined from the slopes of the $\ln(\rho/T) \rightarrow 1/T$ and $\alpha e/k \rightarrow 1/T$ plots show that for $CuCr_2O_4$ the major contribution to E_a (total activation energy) is from E_μ.

Figure 2 shows that as Al^{3+} is introduced the nature of the $\log(\sigma T) \rightarrow 1/T$ plot remains unaltered, but Fig. 4 clearly shows that the Seebeck coefficient for substituted tetragonal samples, NA1, NA2, NA6 (except NA8), and for all the cubic samples (except NA10) becomes negative. n-type conduction in the substituted spinels could be due either to oxygen deficiency or to the presence of lower valent cations in the spinel lattice. As De et al. have shown that annealing of the samples in air produces an oxygen excess in $CuCr_2O_4$, oxygen deficiency in the substituted samples is unlikely to occur. Hence, n-type conduction in these samples seems to be due to the presence of lower valent cations. Studies of several substituted spinel oxides, viz., $Mg_{1-x}Mn_{3-x}O_4$ (11) and $Ni_{1-x}Mn_{2+x}O_4$ (12),

have shown that when substitution alters the cation distribution of the spinel, there is a likelihood of alteration in the valency of one of the cations. In $CuCr_{2-x}Al_xO_4$ it has been established that as x is increased the cation distribution changes. Hence on introduction of Al^{3+} ions to the tetrahedral sites the Cu_{tet}^{2+} ions are probably reduced to a lower valent ion, i.e., Cu^{1+}. Thus the tetrahedral sites would be occupied by Cu^{1+}, Cu^{2+}, and Al^{3+} ions and conduction would be by charge hopping between Cu_{tet}^{2+} and Cu_{tet}^{1+}. Studies of $Cu_{1-x}Mg_xCr_2O_4$ and $Cu Cr_{2-x}Rh_xO_4$ (4) in which the cation distribution is not changed by substitution show that introduction of Mg^{2+} or Rh^{3+} ions does not alter the conduction type in these spinels. This further confirms that a change from p-type to n-type conduction on Al^{3+} substitution is related to the $CuCr_2O_4$ becoming partially inverse with the introduction of Al^{3+} ions.

Along with n-type conduction, p-type conduction due to charge hopping between Cr_{oct}^{3+} and Cr_{oct}^{4+} will simultaneously occur as Cr^{4+} ions will also be present as impurities in the substituted samples. Under these conditions the observed conduction will depend on the relative amount of Cu_{tet}^{1+} present, i.e., the amount of Al^{3+} on the tetrahedral site. When $Al_{tet}^{3+} < 0.4\%$, p-type conduction is expected and for $Al_{tet}^{3+} > 0.4\%$, n-type. In NA2 $Al_{tet}^{3+} = 0.06$ and for NA1 it is less than 0.06. The exact cation distribution for NA1 has not yet been computed but its n-type nature implies that its Al_{tet}^{3+} is greater than 0.4%. Compounds with $x = 0.08, 0.06, 0.04,$ and 0.02 were prepared and they were all found to be p-type. The presence of both types of charge carriers in aluminum-substituted samples seems to be quite likely in view of the results of the thermoelectric power measurements on NA8 and NA10. It is apparent from Fig. 5 that NA8 is p-type below 380 K and n-type above 392 K. Such a change from hole conduction to electron conduction at a particu-

lar temperature can occur only if both types of charge carriers are present in the semiconductor and n-type or p-type behavior will depend on the charge carriers which dominate at a particular temperature.

n-type conduction due to charge hopping between tetrahedral site cations is expected to require more activation energy than that due to charge hopping between octahedral site ions as the distance between octahedral site ions is smaller than the distances between tetrahedral site cations in the spinel lattice. This implies that E_a (NA1) should be greater than E_a (NA0) and this is observed in the results (Table I). Hopping conduction involving tetrahedral site ions has also been found by Gillot et $al.$ (13) in aluminum-substituted $FeCr_2O_4$.

The disappearance of tetragonal distortion in the $CuCr_{2-x}Al_xO_4$ system occurs for considerably high values of Cu_{tet}. Studies by De et $al.$ have shown that when Cu_{tet} is 0.78 the distortion is absent while the values are 0.4 in $Cu_{1-x}Mg_xCr_2O_4$ (4) and 0.65 in $CuCr_{2-x}Fe_xO_4$ (14). The higher values in the Fe- and Al-substituted spinels could be due to the simultaneous presence of copper ions on both sites, giving distortion in opposite directions. But comparison of the values of these two compounds reveals that in the aluminum-substituted spinel the value is higher than that in the iron-substituted spinel. This suggests that all the copper on the tetrahedral site in $CuCr_{2-x}Al_xO_4$ is probably not present as Cu^{2+} J–T ion and hence does not contribute fully to the cooperative J–T effect. This is possible if some of the copper is present as the non-J–T Cu^{1+} ion. Finally, the presence of Cu^{1+} ions was confirmed by the results of ESCA measurements. The spectrum shows the presence of Cu^{1+} ions in the aluminum-substituted $CuCr_2O_4$ samples but not in $CuCr_2O_4$.

TEP of the samples with $x > 1.0$ show them to be n-type in the temperature range studied. γ_0 calculations for NA16 show that the values are below the optical phonon fre-quencies. This probably indicates that with increasing Al content the hopping sites are separated from each other by Al ions which is also reflected in the increase in E_μ values in the Al-rich samples. The calculated μ values which are rather small for all the compounds also show an increase with the value of x.

Further studies are being carried out to investigate the cause for an increase in the Seebeck coefficient with temperature.

Conclusion

From these results it may be concluded that the p-type conduction in $CuCr_2O_4$ is due to the presence of Cr^{4+} ions on the octahedral sites. On substitution of Al^{3+} for Cr_{oct}^{3+} in $CuCr_2O_4$ the Al^{3+} and Cu_{tet}^{2+} ions are distributed between the two sites of the spinel lattice. The presence of Al_{tet}^{3+} reduces Cu^{2+} to a lower valent state and both Cu^{2+} and Cu^{1+} are present on the tetrahedral site. n-type conduction in the substituted compounds is due to electron hopping between Cu_{tet}^{2+} and Cu_{tet}^{1+}. Simultaneously octahedral site hole conduction due to charge hopping between Cr^{3+} and Cr^{4+} ions also occurs. The samples show n-type or p-type behavior depending on the dominant charge carrier present at a particular temperature.

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