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BRIEF COMMUNICATION

Studies on Compensated Cu–Cr–Al Spinel Oxide Semiconductors

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Electrical resistivity (ρ) and thermoelectric power (α) measurements were carried out in air on $CuCr_{2-x}Al_xO_4$ ($0.06 \leq x \leq 0.10$) spinel oxides in the temperature range 300–675 K. Carrier concentration (n), optical phonon frequency (γ_o), and mobility (μ) values have been calculated from resistivity and thermoelectric power data. The results show that $CuCr_{2-x}Al_xO_4$ spinel oxides are compensated semiconductors and the total compensation of the hole carriers by electrons occur when 0.09 chromium ions are replaced by aluminium ions. © 1995 Academic Press, Inc.

INTRODUCTION

The spinel oxide $CuCr_2O_4$ is a p-type semiconductor. Earlier studies have shown that on substituting Cr^{3+} by Al^{3+} the samples, $CuCr_{2-x}Al_xO_4$, become n-type (1). The present work seeks to determine the minimum amount of Al^{3+}, i.e., x, required to change p-type $CuCr_2O_4$ to an n-type semiconductor.

EXPERIMENTAL

The solid solutions $CuCr_{2-x}Al_xO_4$ for x = 0.06, 0.08, 0.09, and 0.10 were prepared from stoichiometric mixtures of the respective nitrates by the method described in an earlier paper (2). X-ray diffraction studies of all the samples were carried out using a Philips X-ray diffraction unit (Model PW1710) using Cu$K\alpha$ radiation with Ni filter. Resistivity and thermoelectric power measurements of all the samples were carried out in air in the temperature range 300–675 K following the procedure described elsewhere (1, 3). All the samples were annealed before each measurement to eliminate a grain boundary effect.

RESULTS AND DISCUSSION

Table 1 gives the chemical composition of various aluminium-substituted $CuCr_2O_4$ samples, their code names, optical phonon frequency (γ_o), and mobility (μ) values at 550 K. Resistivity of all the samples followed the exponential law

$$\rho = \rho_o \exp(E_a/kT),$$

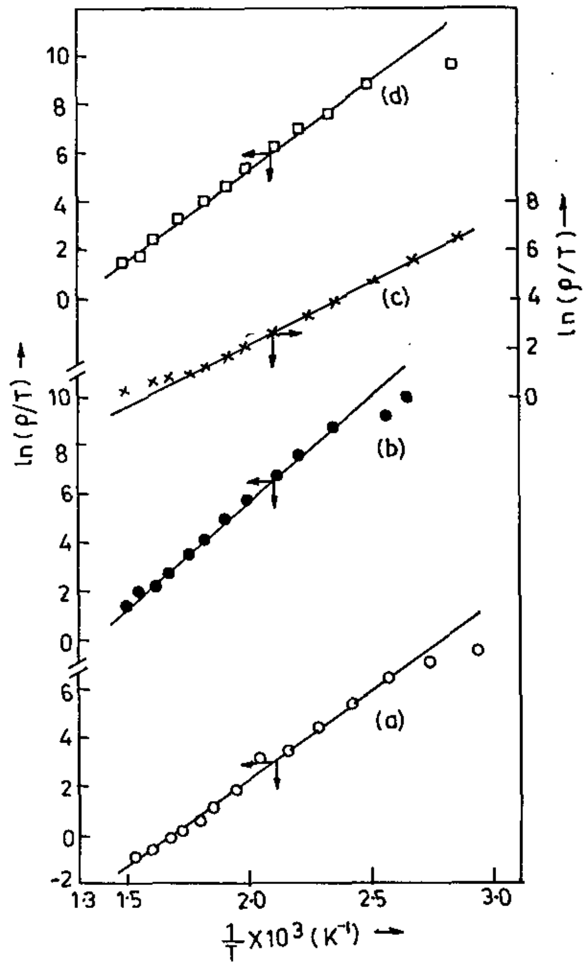

FIG. 1. Plots of ln(ρ/T) vs $1/T$ for (a) NA6, (b) NA8, (c) NA9, (d) NA10.

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TABLE 1
Sample Composition, Code Name, Optical Phonon Frequency (γ_o), and Mobility (μ) for Various $CuCr_{2-x}Al_xO_4$ Samples

Sample composition	Code name	γ_o (sec^{-1})	$\mu_{550 K}$ ($cm^2V^{-1}sec^{-1}$)
$CuCr_{1.94}Al_{0.06}O_4$	NA6	1.19×10^{12}	2.5×10^{-7}
$CuCr_{1.92}Al_{0.08}O_4$	NA8	7.99×10^{12}	1.43×10^{-7}
$CuCr_{1.91}Al_{0.09}O_4$	NA9	5.41×10^{10}	1.96×10^{-7}
$CuCr_{1.90}Al_{0.10}O_4$	NA10	2.42×10^{11}	2.64×10^{-8}

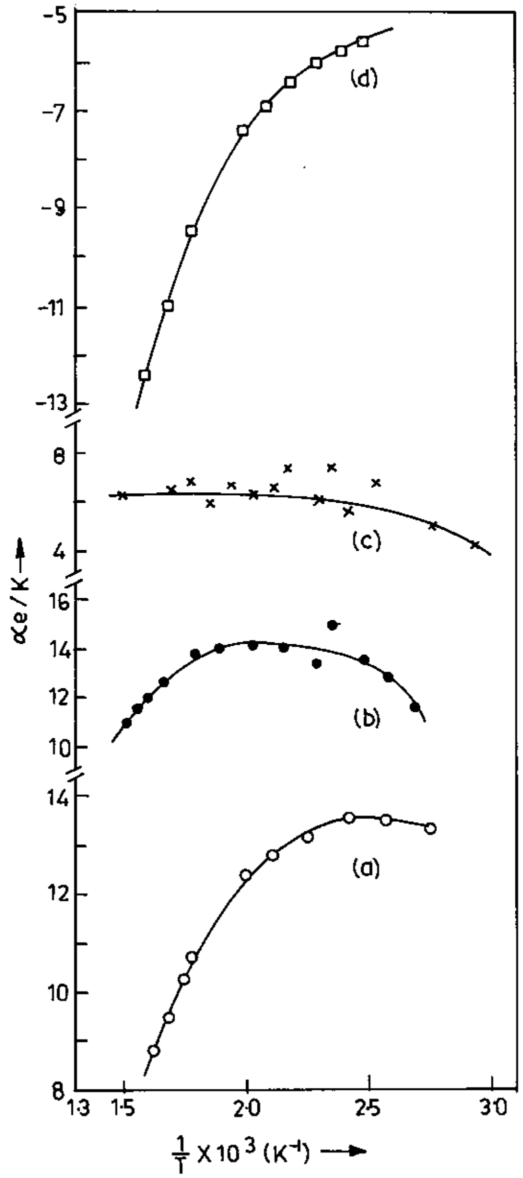

FIG. 2. Plots of $\alpha e/k$ vs $1/T$ for (a) NA6, (b) NA8, (c) NA9, (d) NA10.

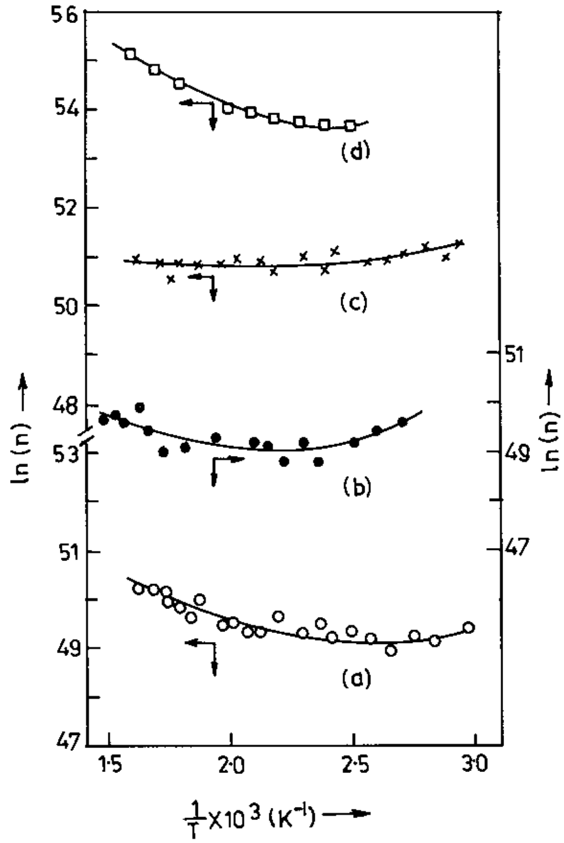

FIG. 3. Plots of ln(**n**) vs $1/T$ for (a) NA6, (b) NA8, (c) NA9, (d) NA10.

in the temperature range studied, where ρ is resistivity in ohm-cm, T the absolute temperature, k the Boltzmann constant, and E_a the thermal activation energy. The $\ln(\rho/T)$ vs $1/T$ plots for all the samples are shown in Fig. 1. From the $\ln(\rho/T)$ vs $1/T$ linear plots, the optical phonon frequency values (γ_o) and mobility values (μ) have been calculated following the method of Metselaar *et al.* (4).

The reduced thermoelectric power α' ($= \alpha e/k$) vs $1/T$ plots for all the samples are shown in Fig. 2. The results show that NA6 is a p-type semiconductor in the temperature range studied whereas NA10 is n-type in the same temperature range. NA8 and NA9 appear n-type at room temperature but on heating change to p-type. Following Basak and Ghose (5), the values of carrier concentration **n** have been calculated from the values of α using the formula

$$\mathbf{n} = Nv \exp(-\alpha/k),$$

where Nv is the density of states involved in the conduction process, k is the Boltzmann constant, and α is the Seebeck coefficient. The plots of ln(**n**) vs $1/T$ are shown in Fig. 3. The plots show that for all the samples except NA9, the carrier concentration remains almost constant up to 500 K and then on heating increases. NA9, however, does not show any change in the carrier concentration in the temperature range studied.

The results show that the $CuCr_{2-x}Al_xO_4$ samples with $x \leq 0.06$ are p-type at room temperature and $x \geq 0.08$ are n-type. The linear $\ln(\rho)$ vs $1/T$, $\ln(\rho/T)$ vs $1/T$, and the calculated γ_o values indicate that all samples are semiconductors where conduction occurs by hopping of charge carriers. Murthy and co-workers (3) have shown that $CuCr_2O_4$ is p-type due to the presence of Cr^{4+} ions in the spinel oxide. From ESCA measurements Padmanaban *et al.* (1) have shown that the Al^{3+} substituted samples contain some Cu^{1+} ions and when these exceed the Cr^{4+} ions present in $CuCr_2O_4$, the samples become n-type and hence $CuCr_{2-x}Al_xO_4$ spinel oxides were considered to be compensated semiconductors. In the present studies the carrier concentrations, **n**, for all the samples were calculated. Figure 3 shows that in NA6 the charge carrier concentration initially remains constant and then increases above 500 K; NA8 shows an initial fall and then **n** increases slightly above 550 K. NA9 shows almost no change in **n** after an initial fall and in NA10, **n** increases with increasing temperature. These results conclusively show that the $CuCr_{2-x}Al_xO_4$ spinel oxides are compensated semiconductors and the total compensation of the hole carriers by electrons occur when 0.09 chromium ions are replaced by aluminium ions.

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