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On some transport properties of strontium-doped lanthanum chromite ceramics*

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D.C. electrical conductivity, Hall mobility and magnetic susceptibility measurements on $La_{1-x}Sr_xCrO_3$ ($0 \leqslant x \leqslant 0.25$) perovskite ceramic system, and their temperature dependence, have been carried out to understand the nature of the transport mechanism in them. The electrical conductivity and Hall mobility displayed thermally activated temperature dependence with activation energies that varied from 0.13 to 0.23 eV. The variation of the d.c. conductivity of the polycrystalline $La_{1-x}Sr_xCrO_3$ with strontium content (X) has been found to be strongly affected by the changes in microstructure. Magnetic susceptibility data indicate that the electronic transport is due to the presence of Cr^{4+} ions in the lattice, and that the localized level of hopping is associated with the chromium 3d band.

1. Introduction

Interest in highly conducting perovskite ceramic systems, such as $La_{1-x}Sr_xCrO_3$, has increased recently because of their important technical applications such as electrodes for magneto hydro-dynamic (MHD) power generation, heating elements for high temperature furnaces, fuel cell interconnects and as materials for furnace linings [1–7]. However, the electronic conduction processes in lanthanum chromite and similar compounds of the transition metals are still the subject of much discussion. This stems from the fundamental problem of why they are not generally metallic conductors, although they have an incompletely filled d band. A combination of a localized and collective electron model has been considered to be appropriate for conduction in lanthanum chromite by Goodenough [8, 9].

Although these materials are polycrystalline in nature, a large degree of localized disorder is present as a result of the random distribution of divalent ions, either on the rare earth site or on the transition metal ion site [2–5]. This random distribution of divalent ions in the lattice not only varies the distance between acceptor states, but also introduces disorder in the lattice. Thus the electrical and magnetic properties of these polycrystalline bodies might be expected to follow the behaviour predicted for amorphous or disordered solids. As such, the characterization of the transport properties of these polycrystalline bodies through a combination of the Hall effect, the resistivity and the susceptibility measurements is as important in understanding the electrical transport properties of these semiconducting materials as it is for the single crystal semiconductors.

2. Experimental details

$La_{1-x}Sr_xCrO_3$ were prepared using the usual ceramic techniques in the form of tablets and toroids. An indium amalgam coating was given on the two circular faces of lapped and cleaned tablets for ohmic contacts [5]. The d.c. bulk resistivity was measured by the usual two probe method. Activation energies of conduction were computed from the slope of the least squares fit of $\log(\sigma T)$ against $(1/T)$ using the relation [10, 11]:

$$\sigma = \frac{\sigma_0}{T} \exp(-E_c/kT) \quad (1)$$

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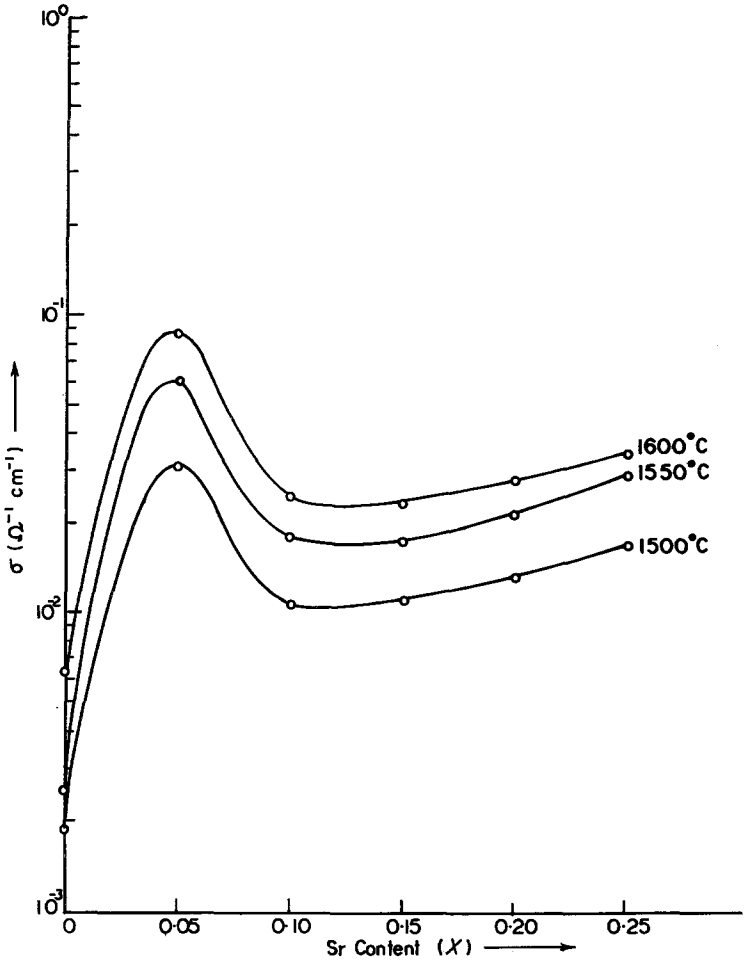

Figure 1 Plot of d.c. conductivity against strontium content in $La_{1-x}Sr_xCrO_3$ compositions sintered at various temperatures for 24 h.

where E_c is the energy required to transfer a carrier between the localized sites, T is the absolute temperature and k is Boltzmann's constant.

The Hall measurements were done on the same sintered circular tablets of diameter D following the Vander Pauw method [12, 13].

The inductance of sintered toroids of average dimensions, $OD = 14$ mm, $ID = 9$ mm, $h = 3$ mm, was measured in a Siemens R 2077 inductance bridge for the magnetic susceptibility measurements.

3. Results

3.1. D.C. conductivity

Fig. 1 shows the variation of the d.c. conductivity of $La_{1-x}Sr_xCrO_3$ as a function of strontium content (X) for different sintering schedules. The conductivity first shows a sharp increase with an increase in the strontium content from $X = 0$ to 0.05. No appreciable change in conductivity at $X = 0.15$ in comparison to $X = 0.10$ is observed. However, a slight increase in conductivity is registered for the composition having a strontium content $X = 0.20$ and 0.25.

An increase in the value of the electrical conductivity with an increase in the sintering temperature is obtained for all the compositions. The variation of conductivity with temperature as (σT) against $(1/T)$ is shown in Fig. 2. The activation energies for various compositions computed from the least squares fit method for these curves are listed in Table I. The values are found to be less for the compositions of higher conductivity.

3.2. Hall mobility

The values of charge carrier concentration for various compositions obtained from Hall measurements are listed in Table I. It is found to be a maximum for the LCS-5 ($X = 0.05$) composition, which also shows the highest conductivity, and its variation with strontium content closely follows the conductivity behaviour exhibited in Fig. 1.

The variation of the Hall mobility with tem-

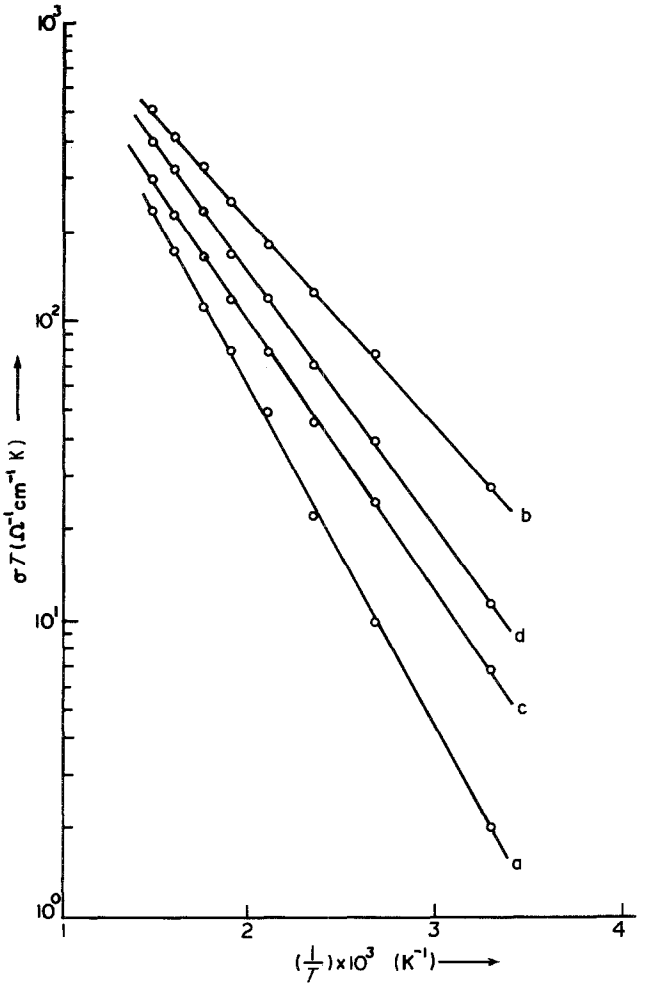

Figure 2 Semilog plot of the product of d.c. conductivity and absolute temperature against $(1/T)$ for (a) LCO, (b) LCS-5, (c) LCS-10 and (d) LCS-25 compositions sintered at 1600° C.

perature as the product $(\mu_H T)$ against $(1/T)$ is plotted in Fig. 3. Using the equation [10, 11]

$$\mu_H = \frac{\mu_0}{T} \exp(-E_H/kT) \quad (2)$$

the activation energies (E_H) for Hall mobilities have been calculated (see Table I). These values are in close agreement with the corresponding values of d.c. conductivity.

3.3. Magnetic susceptibility

Fig. 4 shows the variation of magnetic susceptibility against temperature for $La_{1-x}Sr_xCrO_3$ $(0 \leqslant x \leqslant 0.25)$ ceramic system sintered at 1500 and 1600° C. All samples including that of pure $LaCrO_3$ are found to have a similar temperature dependence of susceptibility above the transition temperature. However, the magnetic sucseptibilities of strontium-doped samples were lower than that of pure $LaCrO_3$ in the studied temperature range. It is also observed that the susceptibility (χ) becomes more and more temperature insensitive as the strontium content increases.

TABLE I Activation energies for d.c. conductivity and Hall mobility and carrier concentration per cc as calculated from Hall measurements

Composition $La_{1-x}Sr_xCrO_3$	Activation energy		Carrier concentration per cc
	d.c. conductivity (eV)	Hall mobility (eV)	
LCO ($x = 0$)	0.229 ± 0.002	0.22 ± 0.002	9.2×10^{19}
LCS-5 ($x = 0.05$)	0.138 ± 0.003	0.121 ± 0.003	1.1×10^{22}
LCS-10 ($x = 0.10$)	0.187 ± 0.004	0.180 ± 0.002	5.6×10^{21}
LCS-25 ($x = 0.25$)	0.178 ± 0.003	0.146 ± 0.005	7.4×10^{21}

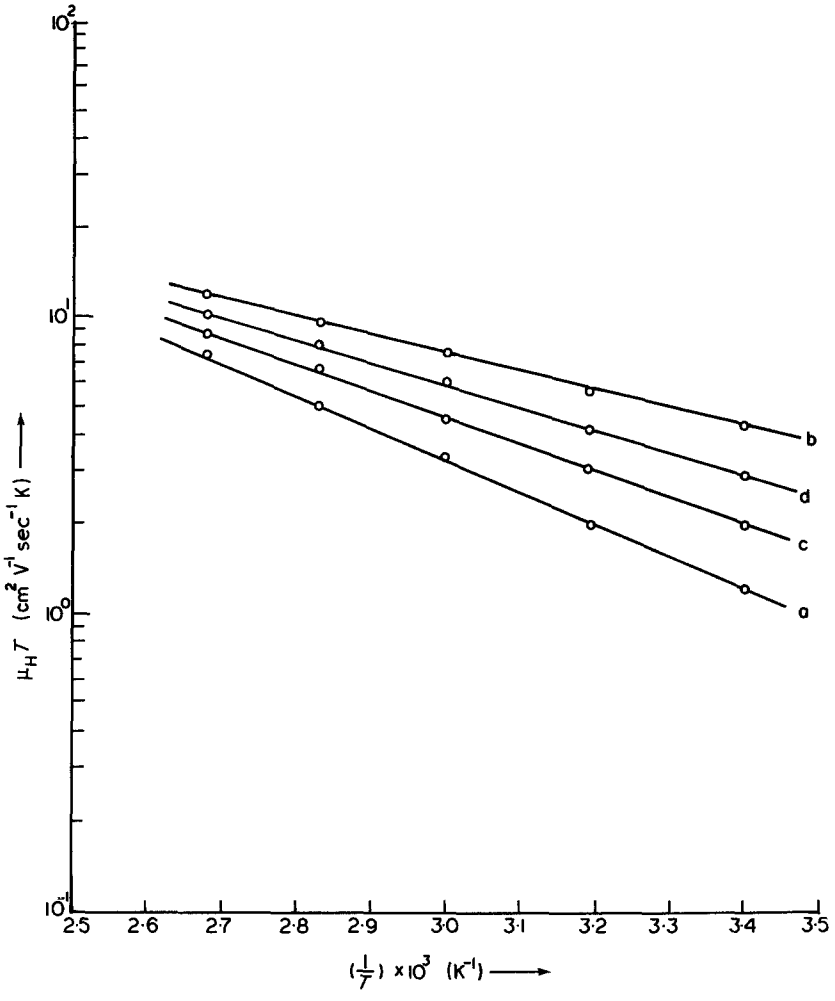

Figure 3 Semilog plot of the product of Hall mobility and absolute temperature against $(1/T)$ for (a) LCO, (b) LCS-5, (c) LCS-10 and (d) LCS–25 compositions sintered at 1600° C.

4. Discussion

In $La_{1-x}Sr_xCrO_3$, Sr^{2+} ions are distributed randomly on the La^{3+} lattice sites. It is generally believed that the charge compensation takes place via the chromium ions ($Cr^{3+} \rightarrow Cr^{4+}$) giving a d-band p-type conductivity [2–5]. A sharp increase in the conductivity at the strontium doping level of $X = 0.05$ (Fig. 1) has been attributed to the formation of Cr^{4+} ions as a result of charge compensation in the lattice and the conduction being caused by the hopping of polarons betweeen Cr^{3+} and Cr^{4+} ions. However, a further increase in the strontium content, i.e. $X \geqslant 0.10$ gives rise to a decrease in conductivity. It may be explained by considering the conductivity as a bulk property dependent on the grain size, density and the microstructure of the material which would influence the conductivity in the following way:

(i) an increase in the grain size will increase the grain conductivity.

(ii) an increase in the density will increase the bulk conductivity by suppressing the preferential oxidation of the grain boundaries during cooling after sintering. Additional strontium, i.e. $X \geqslant 0.10$ (greater than the solubility limit), into the lattice gets segregated at the grain boundaries [14], and thereby increases their effective thickness leading to a decrease in the bulk conductivity. The formation of a high resistance layer at the grain boundaries results in an increase of resistivity [15].

With an increase in strontium doping, i.e. $X \geqslant 0.20$, a slight increase in conductivity is observed. In these compositions, a strontium-rich second phase is found to precipitate along the grain boundaries [16] and also the microstructure exhibits exaggerated grain growth [17]. While the

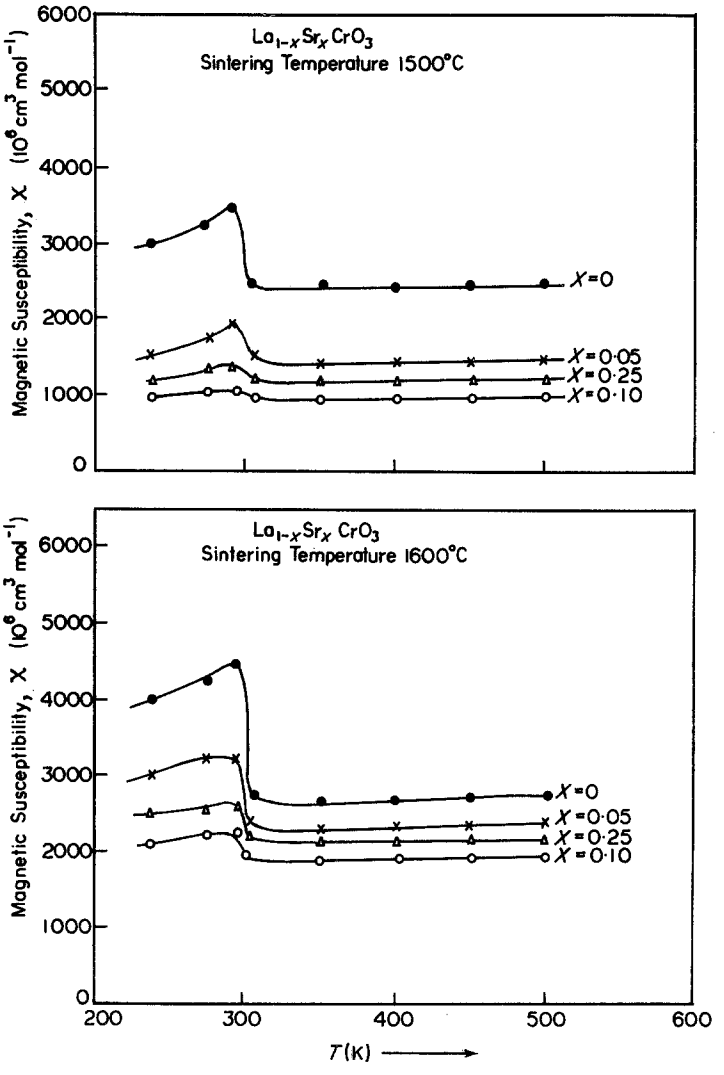

Figure 4 Magnetic susceptibility against temperature for $La_{1-x}Sr_xCrO_3$ system sintered at 1600° C (lower part) and 1500° C (upper part).

former would tend to decrease the conductivity, the overall slight increase in conductivity is mainly due to the presence of larger grains.

The decrease in activiation energy with an increase in the carrier concentration (Table I) is consistent with polaron hopping [18]. Mott [19] showed that as the polarons approach each other and their polarisation clouds start to overlap, the energy required for hopping will be reduced. This view is further reinforced by a thermally activated temperature dependence of the Hall mobility and d.c. conductivity, which are in close agreement, indicating the transport mechanism associated with the hopping of polarons between localized levels.

Although the measurements of susceptibility on all the samples indicate that the material is antiferromagnetic at low temperatures, the shape of both the curves (Fig. 4) at about 300 K is not that of a typical antiferromagnetic material. Interestingly, all the samples, including the pure $LaCrO_3$, have a very similar temperature dependence of the susceptibility above the transition temperature, even though the electrical conductivity varies by two to three orders of magnitude, when the material is doped. However, it is to be noted that the doped samples have a lower magnitude of susceptibility in this high temperature region. Thus in the strontium-doped samples, all the chromium can not be in the 3+ state. Therefore it may be concluded that the concentration of Cr^{3+} ions in the antiferromagnetic lattice is diminished by strontium doping and chromium defects of lower spin are created. Thus the earlier argument that the electronic transport in strontium-doped $LaCrO_3$ is associated with the presence

of Cr^{4+} ions in the lattice is consistent with this picture.

The temperature insensitivities of χ–T curves with larger strontium content (X) could be due to the heterogeneities caused by strontium segregation effects. The presence of compositional heterogeneities across grain and grain boundaries give rise to numerous χ–T curves superimposed to give the one which is comparatively temperature insensitive [20].

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