JOURNAL OF MATERIALS SCIENCE 3 (1968) 389–394

Changes in Valency State of Ions in $CuMn_2O_4$ at High Temperatures

D. B. GHARE, A. P. B. SINHA, L. SINGH
National Chemical Laboratory, Poona, India

Received 26 February 1968

Thin films of copper manganite with three different molar ratios of Cu : Mn *viz* 1 : 1, 1 : 2 and 1 : 3 have been deposited on quartz plates. The electrical conductivity of these thin films has been studied as a function of temperature. The energy of activation for electrical conduction in these compounds is found to increase from 0.20 eV to about 0.62 eV above 600° K. Differential thermal analysis of bulk sample of copper manganite also shows a small endothermic change at 600° K, while thermogravimetric analysis does not show any change in weight. It has been concluded from these results that the stable form of the ionic configuration of copper manganite at low temperatures, i.e. $Cu^{1+}[Mn^{3+}Mn^{4+}]O_4$ changes at high temperatures to $Cu^{2+}[Mn_2^{3+}]O_4$

1. Introduction

The problem of cation distribution and valence state of copper-ions in copper manganite has attracted the attention of several workers. Sinha *et al* [1] studied the crystal structure of copper manganite and found that it has the "normal" spinel structure with cubic symmetry; which suggests that the number of Mn^{3+} ions in copper manganite is less than 1.2 per formula unit [2]. They have explained this behaviour by proposing the ionic formula $Cu^{1+}[Mn^{3+}Mn^{4+}]O_4$. Miyahara *et al* [3] and Miyahara [4] also found that copper manganite has cubic symmetry but they explained this behaviour by suggesting that the directions of distortion caused by Cu^{2+} and Mn^{3+} ions in copper manganite are opposite to each other and therefore these distortions get compensated and the compound shows the cubic symmetry. They therefore suggested the ionic formula of copper manganite to be $Cu^{2+}[Mn_2^{3+}]O_4$.

P. K. Baltzer and E. Lopatin [5] studied the magnetic susceptibility of copper manganite as a function of temperature and found that the experimental C_M values obtained from the $1/\chi$ versus T graph above 600° K match better with the formula $Cu^{2+}[Mn_2^{3+}]O_4$ than with $Cu^{1+}[Mn^{3+}Mn^{4+}]O_4$. Ikuo-Aoki [6] studied this problem with the help of the X-ray diffraction intensity measurements and suggested the cation distribution formula $(Mn_{0.12}Cu_{0.88})[Cu_{0.12}Mn_{1.88}]O_4$. Robbins and Darcy [7] have also studied the ionic distribution in spinels with the help of X-ray and neutron diffraction techniques. They found that the Jahn-Teller distortion and site preference of Cu^{2+} ions are not single-ion properties but are strongly dependent on the other cations present in the spinel.

Recently Blasse [8] has reported his results on the magnetic susceptibility and saturation magnetisation of various spinels containing both copper and manganese ions. He has suggested from his results on $CuMg_{0.5}Mn_{1.5}O_4$ and $CuRhMnO_4$ that the cation distribution in copper manganite at low temperatures can be represented by the formula proposed by Sinha *et al*, *viz* $Cu^{1+}[Mn^{3+}Mn^{4+}]O_4$. At high temperatures, however, the copper ions tend to become divalent and the distribution may then be represented by the formula $Cu^{2+}[Mn_2^{3+}]O_4$.

Such a change of valence state of copper ions at high temperatures must however be accompanied by a corresponding change in the activation energy for the electrical conduction. Sabane *et al* [9] have reported the electrical conductivity of copper manganite as a function of temperature but they have not noticed any break in the conductivity versus reciprocal temperature plot. However, from their results, it can be seen that the resistance of copper manganite at high temperatures is very small (10^{-2} ohms/cm). The measurements on the pellets are therefore subject to uncertainties arising from the variation in lead resistances which may also be of the same order.

We have therefore prepared thin films of copper manganite whose resistance is of the order of $10^3 \Omega$ at 500° K. The electrical conductivity of these samples has been measured as a function of temperature and it has been found that the energy of activation changes from 0.20 eV to about 0.62 eV at temperatures above about 600° K. This marked change in the energy of activation at temperatures above about 600° K supports the transformation $Cu^{1+} + Mn^{4+} \rightarrow Cu^{2+} + Mn^{3+}$ at high temperatures. Differential thermal analysis of a bulk sample of copper manganite also showed an endothermic change at about 600° K, but the thermogravimetric analysis of the same sample did not show any change in weight up to 800° K. These results thus support the above transformation.

2. Experimental Techniques and Results

2.1. Preparation of Thin Film Manganites

Thin films of copper manganite with three different molar ratios of copper to manganese (1:1, 1:2, and 1:3) were prepared by a chemical method. The required oxides were weighed in appropriate proportions on a Mettler semi-microbalance and mixed together. The mixture was dissolved in boiling nitric acid and was diluted by distilled water to a concentration of about 10 mg/cm^3. A quartz plate which was to be used as a substrate, was first polished by fine alundum powder and was then washed with chromic and nitric acids and finally rinsed with distilled water. The plate was then dried and kept on a thick stainless steel plate which was heated by a bunsen burner. The solution was sprayed on the hot quartz plate with the help of a glass spraying gun. The spraying was done intermittently so that the temperature of the quartz plate was always maintained above about 400° C. The spraying operation was continued until an opaque layer of the mixed oxides was formed on the surface of the quartz plate due to the decomposition of the nitrates at high temperatures.

This sample was then heated in an electric furnace at 850° C for two h. The temperature was maintained within $\pm$ 5° C with the help of an automatic temperature controller. The sample was then cooled down slowly to room temperature.

For differential thermal and thermogravimetric analysis, the sample was prepared by heating an equimolecular mixture of AR grade CuO and Mn_2O_3 at 1000° C for several hours. The reacted product was then cooled slowly to room temperature.

2.2. Measurement of Electrical Conductivity

A new sample holder assembly was constructed for the electrical conductivity measurements of these thin films in controlled atmospheres (fig. 1). A glass B_{34} socket was fixed on a silica tube of 1 in. (25.0 mm) diameter with the help of araldite cement. The other end of the silica tube

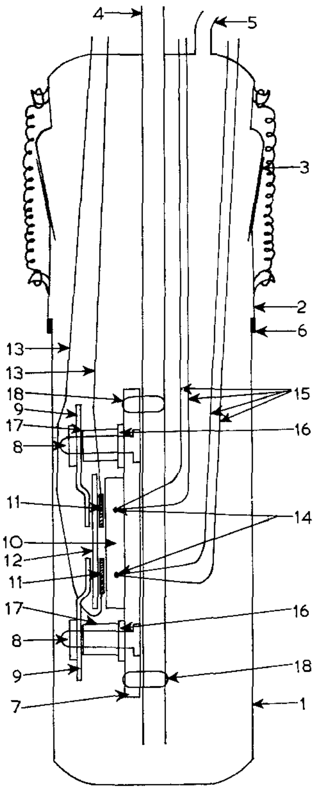

Figure 1 Sample holder assembly for the measurement of electrical conductivity of thin films. *1* Silica tube; *2* glass tube; *3* glass joint; *4* gas inlet tube; *5* gas outlet tube; *6* Araldite cement; *7* silica plate; *8* screws; 9 phosphor bronze springs; *10* sample; *11* platinum foils; *12* mica sheet; *13* platinum lead wires; *14* thermocouples; *15* thermocouple leads; *16* nuts; *17* bushing; *18* nichrome wires.

was fused. A glass cone could be fixed on this socket with the help of silicone grease.

Gas inlet and outlet tubes were provided to maintain the desired atmosphere. The length of the gas inlet tube was so chosen that it went right up to the bottom of the silica tube assembly. Six platinum wires were fused to the glass near the cone joint and platinum foils of appropriate sizes were fused to two of these platinum wires to make the pressed contacts on the surface of the film. Two sets of calibrated chromel/alumel thermocouples were attached to the remaining four platinum wire leads. All wires were insulated from each other with the help of porcelain beads.

A silica plate sample holder was constructed by drilling four holes in a flat silica plate. Two stainless steel screws were fixed in the middle holes by stainless steel nuts. A phosphor bronze strip bent in ~ form was fixed to the screw attached to the silica plate. This strip was used to apply a pressure contact. The sample was then kept on the silica plate holder and the platinum foil contacts were placed at proper positions. A mica piece was then placed above the platinum foils as an insulation between the phosphor bronze springs and the platinum foils. The sample was then fixed tightly on the silica plate holder by tightening the nuts above the phosphor bronze springs. The two thermocouples T_1 and T_2 were placed at the two ends of the sample. The silica plate sample holder was then fixed tightly to the central glass gas inlet tube with the help of the two holes drilled at the end of the silica plate and with two small pieces of nichrome wires. This whole assembly was then introduced into the silica tube through the glass socket as shown in fig. 1. This silica tube assembly was then introduced into the furnace up to a chosen length so that the sample remained in the zone of uniform temperature. The required atmosphere was maintained by passing the desired gas through the assembly. The gas was purified and dried by passing it over and bubbling through suitable chemicals.

Contacts on the surface of the manganite films were made by rubbing soft and pure graphite rods until a low resistivity uniform layer of graphite was formed on the surface of the films. Gold paint was then applied above these graphite contact layers to lower the contact resistance and to protect the graphite contacts from oxidation at high temperatures. The gold paint was dried and reduced to conducting metallic film by heating with an infrared lamp.

Measurements of electrical conductivity as a function of temperature were carried out in the range from room temperature to about 400° C. The uniformity of temperature along the length of the samples was confirmed by measuring the temperature on both the thermocouples T_1 and T_2 which were found to be equal. The graphs of log R versus T for all the three samples are shown in figs. 2 and 3. Since the thickness of the films could not be measured very accurately, the specific resistance values of the samples were not calculated. The energy of activation of the sample was however calculated from the slopes of the graphs of log R versus $1/T$.

It can be seen from figs. 2 and 3 that the points on the graphs of log R versus $1/T$ are located in two straight lines with differing slopes in the two temperature ranges. This indicates that in both these ranges the samples obeyed the relationship $R = R_0 \, e^{\Delta E/kT}$. The change in the slope of the straight line graph of log R versus $1/T$ above a certain temperature indicates that the energy of activation in these two ranges of temperature are different.

The results of the electrical conductivity measurements are tabulated in table I.

2.3. DTA Studies of Copper Manganite

Differential thermal analysis of a bulk sample of

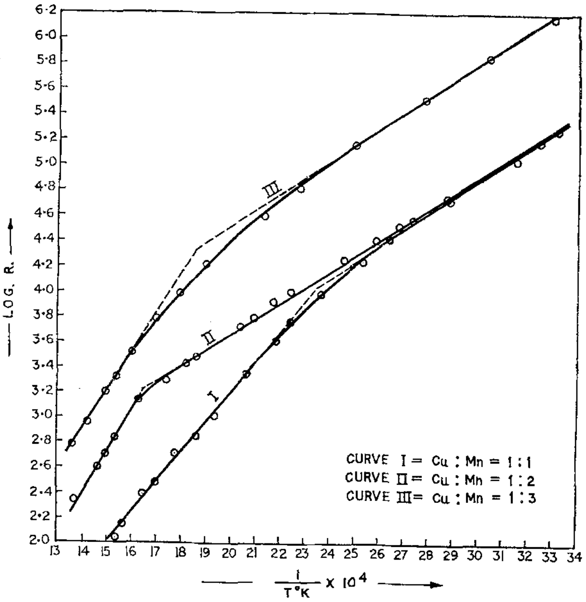

Figure 2 Variation of log R as a function of reciprocal temperature for thin film copper manganites in N_2 atmosphere.

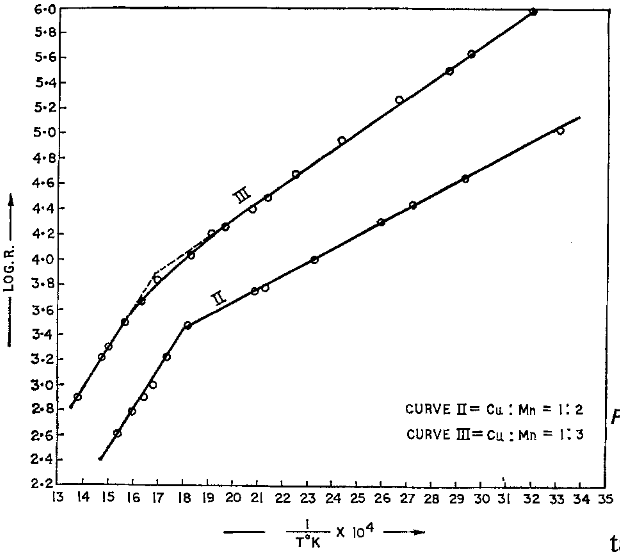

Figure 3 Variation of log *R* as a function of reciprocal temperature for thin film copper manganites in O_2 atmosphere.

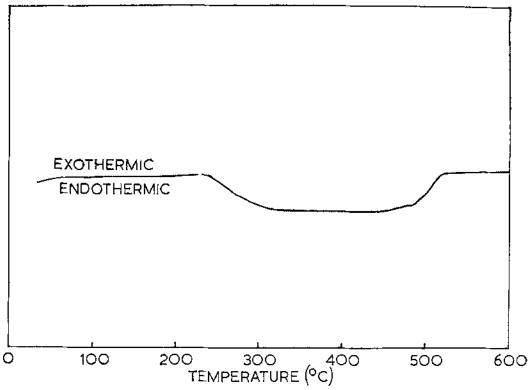

Figure 4 DTA curve of bulk copper manganite.

copper manganite was carried out using a sensitive recorder with 1 mV range. The DTA curve (fig. 4) at the heating rate of about 5° C/min shows a small endothermic change at 500° K. This enthalpy change was not found to be accompanied by any change in weight when the sample of copper manganite was studied thermogravimetrically using a sensitive quartz balance.

3. Discussion

The energy of activation of our thin film samples at temperatures below about 500° K are matching with that obtained by Sabane *et al* [9] for their bulk copper manganite samples. It is, however, clear from figs. 2 and 3 that there is a certain transition temperature below which the samples exhibit lower activation energy and above this temperature the samples exhibit high activation energy.

The electrical conduction in manganites takes place through the hopping of the charge carriers from one octahedral site to another [9, 10]. It is also well known that in oxidic semiconductors, the energy of activation for electrical conduction depends on the number of charge carriers [11, 12]. The energy of activation decreases as the number of charge carriers increases and vice versa.

In the distribution $Cu^{1+}[Mn^{3+}Mn^{4+}]O_4$ the number of Mn^{3+} ions is equal to the number of Mn^{4+} ions. The number of charge carriers is therefore large and hence the energy of activation for this type of distribution should be low. But in the case of the distribution $Cu^{2+}[Mn_2^{3+}]O_4$ all the octahedral positions are occupied by Mn^{3+} ions and therefore the number of charge carriers are expected to be very small and hence the energy of activation for this type of distribution should be high.

The high activation energy exhibited by our samples at high temperatures can therefore be explained by assuming that the following transformation may be taking place at high temperatures $Cu^{1+} + Mn^{4+} \rightarrow Cu^{2+} + Mn^{3+}$. The stable form of copper manganite at temperatures

TABLE I Results of the conductivity measurements on thin film manganites.

Composition	Atmosphere	Energy of activation (eV)		
		Low temperature range	High temperature range	Transition temperature (° K)
I Cu:Mn = 1:1 $Cu_{1.5}Mn_{1.5}O_4$	Nitrogen	0.25	0.47	~425
II Cu:Mn = 1:2	Oxygen	0.22	0.64	~550
$Cu\,Mn_2O_4$	Nitrogen	0.25	0.67	~600
III Cu:Mn = 1:3	Oxygen	0.28	0.62	~600
$Cu_{0.75}Mn_{2.25}O_4$	Nitrogen	0.25	0.62	~600

TABLE II Energy of activation and cation distribution in various manganites.

Compound	Cation distribution	Energy of activation ΔE in eV	Reference
$CdMn_2O_4$	$Cd^{2+}[Mn_2{}^{3+}]O_4$	0.73	13
$MgMn_2O_4$	$Mg^{2+}[Mn_2{}^{3+}]O_4$	0.48	13
$CoMn_2O_4$	$Co^{2+}[Mn_2{}^{3+}]O_4$	0.61	13
$ZnMn_2O_4$	$Zn^{2+}[Mn_2{}^{3+}]O_4$	0.49	13
$CuMn_2O_4$	$Cu^{1+}[Mn^{3+}Mn^{4+}]O_4$ (low temp)	0.26	9
$ZnNi_{0.7}Mn_{1.3}O_4$	$Zn^{2+}[Ni_{0.7}{}^{2+}Mn_{0.6}{}^{3+}Mn_{0.7}{}^{4+}]O_4$	0.36	14
$ZnLi_{0.5}Mn_{1.5}O_{3.38}$	$Zn^{2+}[Li_{0.5}{}^{1+}Mn_{0.74}{}^{3+}Mn_{0.76}{}^{4+}]O_{3.88}$	0.37	10

higher than ~ 600° K may therefore be $Cu^{2+}[Mn_2{}^{3+}]O_4$. It can also be seen from table II that the manganites containing only Mn^{3+} ions at the octahedral sites have an activation energy in the range 0.5 to 0.7 eV, while those containing both Mn^{3+} and Mn^{4+} ions at octahedral sites exhibit low activation energy.

The fact that the energy of activation of the copper manganite samples at high temperatures is about 0.62 to 0.67 eV supports the cation distribution formula of copper manganite at these high temperatures of $Cu^{2+}[Mn_2{}^{3+}]O_4$. Magnetic susceptibility results of Blasse [8] on $CuMg_{0.5}Mn_{1.5}O_4$ and $CuRhMnO_4$ would also be consistent with these transformations. The cation distribution formulae of our three copper manganite samples in the low and high temperature regions can therefore be written as shown in table III.

From table III, we can also see that at high temperatures the compounds $CuMn_2O_4$ and $Cu_{0.75}Mn_{2.25}O_4$ possess only Mn^{3+} ions at their octahedral sites. In the case of the compound $Cu_{1.5}Mn_{1.5}O_4$, however, there exists some concentration of Mn^{4+} ions at the octahedral sites even at high temperatures. Therefore, at high temperatures the compounds $CuMn_2O_4$ and $Cu_{0.75}Mn_{2.25}O_4$ should possess higher activation energy as compared to that of the compound $Cu_{1.5}Mn_{1.5}O_4$. Our experimental results are in good agreement with these expectations. At low temperatures the activation energy of all of our compounds are almost equal. At high temperatures, however, the energy of activation of the compounds $CuMn_2O_4$ and $Cu_{0.75}Mn_{2.25}O_4$ is of the order of 0.62 eV while that for the compound $Cu_{1.5}Mn_{1.5}O_4$ is only 0.47 eV.

The transition temperature is also lower in the case of compound $Cu_{1.5}Mn_{1.5}O_4$. The break in the curve of log R versus $1/T$ for this compound appears near about 450° K while in the case of the compounds $CuMn_2O_4$ and $Cu_{0.75}Mn_{2.25}O_4$ the break appears near about 600° K.

Conclusion

The results of electrical conductivity, differential thermal analysis, and thermogravimetric analysis have indicated that in copper manganite there is a transformation $Cu^{1+} + Mn^{4+} \rightleftarrows Cu^{2+} + Mn^{3+}$ taking place at 600° K. At low temperature the structure is close to $Cu^{+1}[Mn^{3+}Mn^{4+}]O_4$ and at temperatures greater than 600° K it is $Cu^{2+}[Mn_2{}^{3+}]O_4$.

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TABLE III Expected cation distribution formulae of our three copper manganite samples.

Compound	Low temperatures	High temperatures
I $Cu_{1.5}Mn_{1.5}O_4$	$Cu^{1+}[Cu_{0.5}{}^{2+}Mn_{1.5}{}^{4+}]O_4$	$Cu^{2+}[Cu_{0.5}{}^{2+}Mn^{3+}Mn_{0.5}{}^{4+}]O_4$
II $CuMn_2O_4$	$Cu^{1+}[Mn^{3+}Mn^{4+}]O_4$	$Cu^{2+}[Mn_2{}^{3+}]O_4$
III $Cu_{0.75}Mn_{2.25}O_4$	$Cu_{0.75}{}^{1+}Mn_{0.25}{}^{2+}[Mn_{1.25}{}^{3+}Mn_{0.75}{}^{4+}]O_4$	$Cu_{0.75}{}^{2+}Mn_{0.25}{}^{2+}[Mn_2{}^{3+}]O_4$

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