

# Defects and electrical conduction in mixed lanthanum transition metal oxides

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Lanthanum and transition metal mixed oxides form an interesting series of compounds with a general formula  $\text{LaMO}_3$  (with  $M = \text{Ti, V, Mn, Cr, Co, Ni}$  and  $\text{Fe}$ ). These compounds have been investigated by many workers as regards to their various physical parameters including the electrical conductivity. The new data reported in this paper refer to the Seebeck coefficient ( $S$ ) in the temperature interval 300 to 1250 K. Electrical conductivity as a function of temperature has also been reported in the same temperature range and this is quite consistent with the values reported in the literature. Using these and other relevant data reported in the literature it has been concluded that native defects are mainly responsible for the electrical conduction in these solids. The nature of defect centres, charge carrier and their electrical transport mechanism is briefly discussed.

## 1. Introduction

Mixed oxides of lanthanum and iron group elements of the form  $\text{LaMO}_3$  ( $M$  stands for iron group elements) have perovskite structure [1, 2] and have been of interest due to their interesting physical properties.  $\text{LaNiO}_3$  and  $\text{LaTiO}_3$  have metallic conductivity and show Pauli-paramagnetism [3].  $\text{LaMnO}_3$  [4, 5],  $\text{LaFeO}_3$  [6, 7] and  $\text{LaCrO}_3$  [8-10] are semiconductors.  $\text{LaCoO}_3$  behaves [10, 11] as semiconductor but becomes metal above 1210 K. Seebeck coefficient data, which are useful in explaining the conduction mechanism, have not yet been published for any of these materials. Prompted by interesting properties of these materials and the lack of Seebeck coefficient data on them, we decided to study the Seebeck coefficient of these materials and to look at the electrical transport mechanism in the light of these data. These studies in a summarized form are reported in this paper.

## 2. Material preparation, characterization and experimental technique

$\text{LaMO}_3$  ( $M = \text{Cr, Fe, Co}$  and  $\text{Ni}$ ) were prepared by solid-state reaction between  $\text{La}_2\text{O}_3$  and  $\text{M}_2\text{O}_3$  at elevated temperature. For the preparation of compounds of the remaining two transition metals ( $M = \text{Ti}$  and  $\text{Mn}$ ) the solid-state reaction between  $\text{La}_2\text{O}_3$  and  $\text{MO}_2$  was carried out. These materials were characterized by XRD patterns and their reported structure. All the peaks observed were identified, ensuring no unreacted starting material left in the final product. Electrical conductivity ( $\sigma$ ) and Seebeck coefficient ( $S$ ) measurements were done using the procedure described elsewhere [12-14].

## 3. Results and discussion

The measurements of  $\sigma$  and  $S$  have been performed on pressed pellets. Air pores and grain-boundary effects

have been considerably reduced using fine-grained powders, higher pelletizing pressure and annealing the pellet at higher temperature for longer time ( $\sim 40$  h). Appropriate corrections were applied for pore fraction. The variation of Seebeck coefficient with temperature for all these compounds is shown in Fig. 1. The summarized results of  $\sigma$  and  $S$  measurements are given in Table I. In all these mixed oxides, current density is independent of time even at elevated temperatures and higher electric fields. Furthermore, d.c. values of  $\sigma$  have been found higher than the corresponding a.c. values at all temperatures. These observations indicate that these solids are essentially electronic conductors. The electronic conduction in solids is usually explained by a broad energy band model. It has been discussed in detail elsewhere [15] that intrinsic band conduction in these solids will involve an energy greater than 1 eV. Observed activation energies in  $\sigma$  are, however, quite low. Therefore intrinsic band conduction in these solids is ruled out. It is observed from Table I that the slope of the  $S$  against  $T^{-1}$  plot for the studied compounds, except  $\text{LaTiO}_3$  and  $\text{LaNiO}_3$ , is very small in comparison to activation energy observed from the conductivity data. The large difference in energies suggests that the mobility of the charge carrier is thermally activated. This rules out even extrinsic band conduction in these solids. The constancy of  $S-T^{-1}$  plots indicates that the number of charge carriers in these solids is constant and independent of temperature. This may happen only when charge carriers are localized on defect centres which are inherently present in these solids and are not thermally generated. It is well known that transition elements are multivalent and it has been suggested [6, 8] that there may exist a large number of  $M^{4+}$  (or  $M^{2+}$ ) centres in these solids due to native defects. The sign of the Seebeck coefficient gives directly the nature of the charge carrier. In the convention used by us, the sign of the charge carrier is

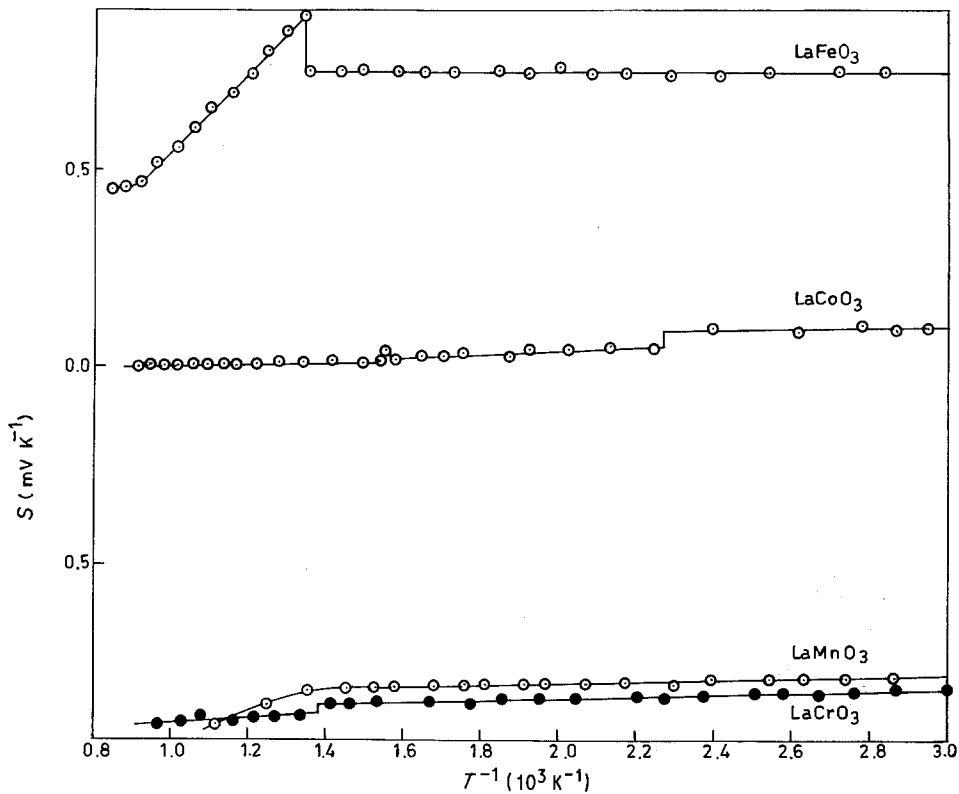


Figure 1 Plot of Seebeck coefficient ( $S$ ) against inverse of absolute temperature ( $T$ ) for  $\text{LaMO}_3$  (with  $M = \text{Mn, Cr, Co and Fe}$ ).

opposite to the sign of  $S$ . On this basis the sign of the entity of the charge carrier has been determined and is given in the Table I. It is seen from this table that the entity of the charge carrier in  $\text{LaFeO}_3$  and  $\text{LaCoO}_3$  is an electron. Therefore, they should have  $\text{Fe}^{2+}$  and  $\text{Co}^{2+}$  defect centres in them. The divalent state of iron and cobalt is the common valence state of these two elements and hence the existence of such centres are quite natural. In the case of  $\text{LaCrO}_3$  and  $\text{LaMnO}_3$  the charge carriers are holes. This suggests the existence of  $\text{Cr}^{4+}$  and  $\text{Mn}^{4+}$  defect centres, respectively, in these solids. The existence of such centres in the above mentioned solids has already been suggested by other workers. The mobility of charge carriers is thermally activated. Therefore, in general, the conduction mechanism in these solids is due to a hopping of charge

carriers from  $M^{4+}$  (or  $M^{2+}$ ) to normal  $M^{3+}$  sites. The cases of  $\text{LaTiO}_3$  and  $\text{LaNiO}_3$  are quite different.  $\sigma$  and  $S$  in the case of hopping conduction are given by the relations

$$\sigma T = \frac{ne^2 v_0^2 a_0^2}{k} \exp(-E_a/kT) \quad (1)$$

$$S = \frac{k}{e} \ln \left( \frac{N_s}{n} - 1 \right) \quad (2)$$

where  $n$  is the number of defect centres per unit volume,  $e$  is the electron charge,  $a_0$  is the average distance between defect centre and a neighbouring  $M^{3+}$  ion,  $v_0$  is the hopping frequency,  $E_a$  is the activation energy and  $N_s$  is the average number of  $M^{3+}$  ions per unit volume.

TABLE I Summary of results of  $\sigma$  and  $S$  measurements on  $\text{LaMO}_3$

Compound	$\sigma$ Measurements; $\sigma T = A \exp(E_a/kT)$					$S$ Measurements; $S = \eta/eT + H$					
	Temp. range (K)	Activation energy, $E_a$ (eV)	Constant, $A$ ( $\Omega^{-1} \text{m}^{-1} \text{K}$ )	Break temp., $T_B$ (K)	Conductivity at 1000 K ( $\Omega^{-1} \text{m}^{-1}$ )	Slope, $\eta$ (eV)	Intercept, $H$ (mV $\text{K}^{-1}$ )	Temp. range (K)	Break temp., $T_d$ (K)	Charge carrier	
$\text{LaTiO}_3$	330–540	0.04	$5.40 \times 10^{-4}$	580	–	–	–	–	–	e	
	540–950	non-linear peaks at 615 K and minima at 835 K			950	–	–	–	750, 835, 950	h	
$\text{LaCrO}_3$	950–1175	1.41	$6.70 \times 10^5$	–	$6.31 \times 10^{-5}$	–	–	–	–	e	
	320–740	0.33	$1.19 \times 10^5$	740	–	0.02	–0.89	320–725	725	h	
$\text{LaMnO}_3$	740–1100	0.28	$5.87 \times 10^4$	–	2.11	0.12	–1.05	725–1100	–	h	
	330–560	0.44	$2.51 \times 10^4$	560	–	0.02	–0.85	350–720	720	h	
$\text{LaFeO}_3$	560–725	non-linear rise			725	–	–	–	–	h	
	725–1250	0.20	$3.61 \times 10^4$	–	3.76	non-linear decrease		720–935	–	h	
$\text{LaCoO}_3$	320–745	0.40	$1.05 \times 10^5$	745	–	0.00	+0.75	330–745	715	e	
	745–1200	0.34	$4.37 \times 10^4$	–	$8.32 \times 10^{-1}$	1.00	–0.45	745–1100	–	e	
$\text{LaCrO}_3$	330–415	0.20	$2.08 \times 10^4$	415	–	0.01	+0.07	330–440	440	e	
	415–540	non-linear rise			540	–	0.05	–0.06	440–640	640	e
	540–1250	0.06	$9.53 \times 10^3$	–	3.72	0.02	–0.02	650–1100	–	e	

TABLE II Calculated values of  $N_s$ ,  $n$  and  $S$  together with the experimental values of  $S$

Compound	$a_0$ (nm)	$N_s$ ( $10^{-28} \text{m}^{-3}$ )	$n$ ( $10^{-24} \text{m}^{-3}$ )	$S$ (mV K $^{-1}$ )	
				calc.	Expt.
LaCrO $_3$	0.482	1.71	5.88	0.70	0.82
LaMnO $_3$	0.489	1.64	0.48	0.90	0.85
LaFeO $_3$	0.488	1.65	5.18	0.70	0.75
LaCoO $_3$	0.474	1.79	1.36	0.82	0.09

The crystal structure of LaMO $_3$  is well known, so one can evaluate the value of  $a_0$ ;  $v_0$  lies between  $10^{13}$  and  $10^{14}$  Hz and hence it can be taken as  $5 \times 10^{13}$  Hz.  $\sigma T$  and  $E_a$  are known from experimental data. Thus using Equation 1, approximate value of  $n$  can be calculated. The values of  $N_s$  can be obtained from the composition and X-ray density of a particular LaMO $_3$ . Knowing  $N_s$  and  $n$  one can determine the value of  $S$  for different LaMO $_3$ . The calculated and experimental values of  $S$  are given in Table II. There is a good agreement between calculated and experimental values of  $S$ . This further strengthens the idea of electrical conduction by hopping of electrons (or holes) localized at defect centres.

The mobility of charge carriers can be evaluated from the relation

$$\mu = \frac{ea_0^2 v_0}{kT} \exp(-E_a^{\mu}/kT) \quad (3)$$

where  $E_a^{\mu}$  is the mobility activation energy expressed by the relation

$$E_a^{\mu} = E_a - e\eta \quad (4)$$

where  $\eta$  is the slope. The results of mobility calculation are given in Table III. It is seen from this table that  $\mu$  lies in the range  $10^{-9}$  to  $10^{-6} \text{m}^2 \text{V}^{-1} \text{sec}^{-1}$  which is quite appropriate for hopping conduction.

Above the lower temperature range,  $\sigma$  has a fast increase in case of LaMnO $_3$  and LaCoO $_3$  and at higher temperature the slope of the log  $\sigma T$  against  $T^{-1}$  curve becomes very small and above 1200 K, almost zero. The case of LaCoO $_3$  has been discussed by many workers [10, 11]. It has been concluded that in LaCoO $_3$  at higher temperatures Co $^{II}$  ( $t_{2g}^6 e_g^1$ ) and Co $^{4+}$  ( $t_{2g}^2 e_g^2$ ) ions are formed by transfer of d electrons from Co $^{3+}$  ( $t_{2g}^4 e_g^2$ ) to Co $^{III}$  ( $t_{2g}^6 e_g^0$ ); Co $^{3+}$ , which are predominantly at the lattice sites, completely disappear and there is a transition of electrons from the localized to the internal state. The conductivity becomes very large and almost metallic. In case of LaMnO $_3$ , the jump is due to transition of electrons from the localized to the itinerant state; but this has to be confirmed by further study. There is a lowering of

TABLE III Mobility of charge carriers for hopping conduction at different temperatures

Compound	Mobility, $\mu(\text{m}^2 \text{V}^{-1} \text{sec}^{-1})$ at		
	400 K	500 K	600 K
LaCrO $_3$	$4.19 \times 10^{-8}$	$2.03 \times 10^{-7}$	$5.60 \times 10^{-7}$
LaMnO $_3$	$1.78 \times 10^{-9}$	$1.62 \times 10^{-8}$	—
LaFeO $_3$	$3.16 \times 10^{-9}$	$2.57 \times 10^{-8}$	$1.01 \times 10^{-7}$
LaCoO $_3$	$1.32 \times 10^{-6}$	—	—

the activation energy in the case of LaCrO $_3$  and LaFeO $_3$  at higher temperatures. However, the Seebeck coefficient still remains almost constant. This indicates that the number of charge carriers is constant and that they continue to have thermally activated hopping mobility. The lowering of the mobility activation energy,  $E_a^{\mu}$ , therefore, is probably brought about by the reduction of potential barrier between Cr $^{4+}$  (Fe $^{2+}$ ) and Cr $^{3+}$  (Fe $^{3+}$ ) sites due to the presence of some holes (electrons) in the thermally excited state of Cr $^{4+}$  (Fe $^{2+}$ ) sites. The reduction of  $E_a^{\mu}$  may also be brought about due to smoothing of the potential barrier by thermal fluctuations, leading to the freeing of holes in an increasing number at higher temperatures. The case of LaCrO $_3$  and other orthochromites has been discussed on similar lines [9].

LaTiO $_3$  is reported [3, 4] to be a metal but we have not found it to be so. The reported crystal structure of this compound is cubic with a lattice parameter 0.393 nm [1]. We have also found it to be cubic but the lattice parameter in our case is 0.788 nm which is about twice the reported value. Our method of preparation of this compound is different from others. Most of the authors [6, 15] have prepared it by taking La $_2$ O $_3$  and Ti $_2$ O $_3$  as starting materials but we have made it by using La $_2$ O $_3$  and TiO $_2$ . Hence the slight oxygen deficiency which is common in titanium oxide, may not be present in our compound. Oxygen-ion deficiency is a source of defect responsible for electrical conduction and this should be very little in our sample. This makes our sample less conducting. The extremely small activation energy involved in  $\sigma$  in the lower temperature range (330 to 540 K) may be due to some donor-type centres or it may be due to moisture. LaTiO $_3$  is a hygroscopic compound which absorbs water when exposed to moist atmospheres. If allowed to absorb moisture, the pellet becomes brittle. Higher-temperature  $\sigma$  and  $S$  variations do not follow any trend.

We have found LaNiO $_3$  to be metallic. This metallic conduction has been investigated by many workers. All have reported this to be metallic due to the collective d-electron behaviour [11].

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