

# Electrical transport in new $\text{La}_{1-x}\text{Nd}_x\text{TlO}_3$ ( $0 \leq x \leq 1$ ) system

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The electrical conductivity ( $\sigma$ ) and thermoelectric power ( $S$ ) for the system  $\text{La}_{1-x}\text{Nd}_x\text{TlO}_3$  ( $0 \leq x \leq 1.0$ ) in the temperature range 295 to 805 K are reported. Both  $\log \sigma$  and  $S$  as a function of  $T$  have been found to be linear with a break in the slope around a specific temperature,  $T_B$ . The break temperature systematically decreases as we proceed from the system  $x = 0$  to  $x = 1.0$ . It has been concluded that conduction below  $T_B$  is extrinsic and takes place owing to hopping of electrons localized on the defect centre  $\text{Tl}^{2+}$  to  $\text{Tl}^{3+}$  on normal sites. Conduction above  $T_B$  is the normal band type in all systems. The energy band gap has been evaluated in all cases and it has been found that it decreases systematically from  $x = 0$  to  $x = 1.0$ .

## 1. Introduction

Mixed metal oxides show interesting chemical and physical properties, some of which have been exploited in technical applications. We have examined the structural, thermal stability, catalytic, magnetic and electrical transport properties of such compounds over the last few years [1-14]. Previously [8, 11], we have reported the syntheses of new mixed metal thallates,  $\text{La}_{1-x}\text{Nd}_x\text{TlO}_3$ , in the solid state.

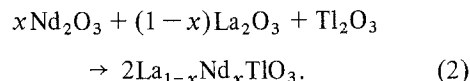
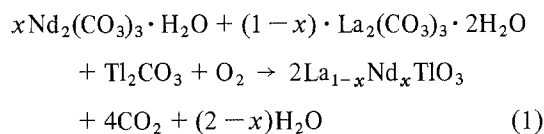
Of the physical properties of solid materials which have been used as heterogeneous catalysts in a variety of chemical industries, electrical conductivity and thermoelectric power are of fundamental importance [15]. The electrical transport of materials is of basic importance in the determination of the relationship between electronic structures and catalytic properties of semiconductors. This paper describes the electrical transport in a new  $\text{La}_{1-x}\text{Nd}_x\text{TlO}_3$  ( $x = 0.0, 0.2, 0.5, 0.8$  and  $1.0$ ) in the temperature range 300 to 805 K.

## 2. Materials and experimental techniques

The materials used were lanthanum carbonate,  $\text{La}_2(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O}$ , lanthanum oxide,  $\text{La}_2\text{O}_3$ , neodymium carbonate,  $\text{Nd}_2(\text{CO}_3)_3 \cdot \text{H}_2\text{O}$ , neodymium oxide,  $\text{Nd}_2\text{O}_3$  (all obtained from Romato materials, India with a stated purity of 99.9%),

thallous carbonate,  $\text{Tl}_2\text{CO}_3$ , and thallic oxide,  $\text{Tl}_2\text{O}_3$  (both obtained from BDH, India of stated purity 99.9%) and acetone (AR).

The  $\text{La}_{1-x}\text{Nd}_x\text{TlO}_3$  were prepared in the solid state using Equations 1 and 2 as given below:



The reaction mixtures were ground thoroughly with acetone (AR) in an agate mortar. The dried reaction mixtures were placed in gold crucibles and heated in a furnace in the presence of air at  $550 \pm 10^\circ\text{C}$  for about 3 h. In all cases, a mixture of black and yellowish brown reaction product was formed first which was finally converted to  $\text{La}_{1-x}\text{Nd}_x\text{TlO}_3$  on cooling, grinding and reheating at a temperature of  $680 \pm 10^\circ\text{C}$  for 7 h. The total period of heating was about 7 h for  $x = 0.0$  and  $1.0$ , and about 10 h for  $x = 0.2, 0.5$  and  $0.8$ .

The structures of all compounds have been obtained by analysing their X-ray diffraction patterns taken using  $\text{CuK}\alpha$  radiation. The lattice parameters of all compounds are given in Table I. The electrical conductivity and thermoelectric

TABLE I Crystal data for  $\text{La}_{1-x}\text{Nd}_x\text{TlO}_3$ 

Sample ( $x$ )	System	Lattice parameters			$d_x^*$ ( $\text{g ml}^{-1}$ )
		$a$ (nm)	$b$ (nm)	$c$ (nm)	
0.0	Orthorhombic	0.616	1.235	0.335	9.37
0.2	Orthorhombic	0.616	1.408	0.335	9.52
0.5	Orthorhombic	0.610	1.219	0.336	9.89
0.8	Orthorhombic	0.597	1.148	0.338	10.26
1.0	Orthorhombic	0.617	1.268	0.335	10.85

\* $d_x$  = X-ray density.

power measurements were carried out on pressed solid pellets using sample holder instruments and a procedure as described elsewhere [10, 16].

### 3. Results

The electrical conductivity,  $\sigma$ , and thermoelectric power,  $S$ , studies were performed on pressed circular pellets because it was difficult to prepare single crystals. In the pelletized materials it is highly desirable to reduce the grain boundaries as much as possible and to obtain a uniform pellet density. This aspect was generally achieved by preparing pellets at very high pressure and sintering them for a sufficiently long time at an appropriate temperature. It is suggested [17] that a highly pressed pellet will acquire a uniform density if its thickness to width ratio is less than 2 (or approximately if  $t^2/a$  is less than 4.0 in the case of circular pellets, where  $t$  is the thickness and  $a$  the cross-sectional area). The pellets used in conductivity and Seebeck coefficient measurements were obtained at a pressure  $8.5 \times 10^8 \text{ N m}^{-2}$  and had ratios of 0.35. This ensured a uniform pellet density,  $d_p$ , which generally lay between 79 and 82% of the theoretical value of crystal density,  $d_x$ , of the corresponding material. A fractional change in the density of pore fraction,  $f$ , given as

$$f = 1 - \frac{d_p}{d_x}, \quad (3)$$

was generally about 0.21.

The presence of grain boundaries greatly affects the transport behaviour of the material. Russel [18] has shown that in such cases the bulk value of the electrical conductivity,  $\sigma$ , can be given by the relation

$$\sigma = \sigma_p \left( 1 + \frac{f}{1 + f^{2/3}} \right), \quad (4)$$

where  $\sigma_p$  is the experimental value of pellet conductivity and  $f$  is given by Equation 3. In order

to verify the applicability of Equation 4, the electrical conductivities of  $x = 0.0$  and 1.0 samples, prepared at different pelletizing pressures were measured and they revealed that the dependence of conductivity on pelletizing pressure,  $P$ , was more pronounced below 520 K and a pore fraction connection, introduced as in Equation 4, did not appear to be very effective. However, above 520 K, the plots of  $\log \sigma$  against  $T^{-1}$  corresponding to  $\sigma$  values at different  $P$  values, were in good agreement. The dependence of  $S$  on  $P$  is difficult to determine because of the relatively large ( $\pm 5\%$ ) error in the experimental value of  $S$ . In this case, no correction for pore fraction has been suggested.

The electric current density,  $J$ , was found to be independent of time for all  $\text{La}_{1-x}\text{Nd}_x\text{TlO}_3$  systems. However, its variation with applied electric field,  $E$ , was linear, in accordance with ohm's law, only for low fields,  $E \leq 30 \times 10^{-2} \text{ V m}^{-1}$  (Fig. 1). At higher fields,  $E \geq 30 \times 10^{-2} \text{ V m}^{-1}$ , the ohmic current is replaced by space charge limited current and the variation of  $J$  with  $E$  does not remain linear.

The a.c. conductivity,  $\sigma_{ac}$ , of all sample pellets at a constant temperature between 290 and 805 K was found to be independent of the applied signal frequency (of  $10^2$  to  $10^4$  Hz). These observations show that grain-boundary effects are insignificant and that  $\sigma_{ac}$  reflects the bulk value of conductivity between  $10^2$  and  $10^4$  Hz. The d.c. conductivity,  $\sigma_{dc}$ , at any given temperature was found to be little higher than the value of  $\sigma_{ac}$  at the same temperature. This supports the view that the lack of additional resistance in practice is due to the absence of grain boundaries; even if they are present their contribution to the resistance is not very effective, presumably because of the highly conductive nature of  $\text{NdTlO}_3$  and easy passage of the charge carriers from one grain to another. In addition, the values of  $\sigma$  for all samples at a par-

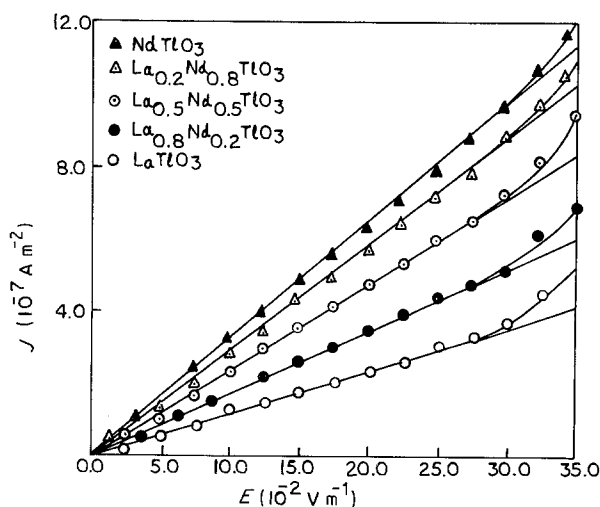


Figure 1 Variation of electric current density,  $J$  ( $\text{A m}^{-2}$ ) with applied field,  $E$  ( $\text{V m}^{-1}$ ).

ticular temperature, or their variation with temperature, do not differ considerably for samples of different thicknesses. The electrode materials (silver paint, silver foil, platinum foil, etc.) were found to have an insignificant effect on the conductivity. However, platinum foil electrodes were preferred for our measurements. The conductivity was also found to be independent of the life of the pellet.

The study of the electrical conductivity and the Seebeck coefficient as a function of temperature is the main feature of the present work. The elec-

trical conductivity was found to depend upon the thermal history of the sample. Its value depends, initially, on heating and cooling cycles, but after a few (20 to 24) hours of heating and cooling cycles, they become repeatable in successive cycles. The repeatable values have been taken as the bulk value of the parameters for the solids. The results of electrical conductivity measurements in the first heating cycle at an a.c. signal frequency of  $10^3$  Hz, are presented as plots of  $\log \sigma$  against  $T^{-1}$  (Fig. 2) in the temperature range studied for all mixed metal thallates. The

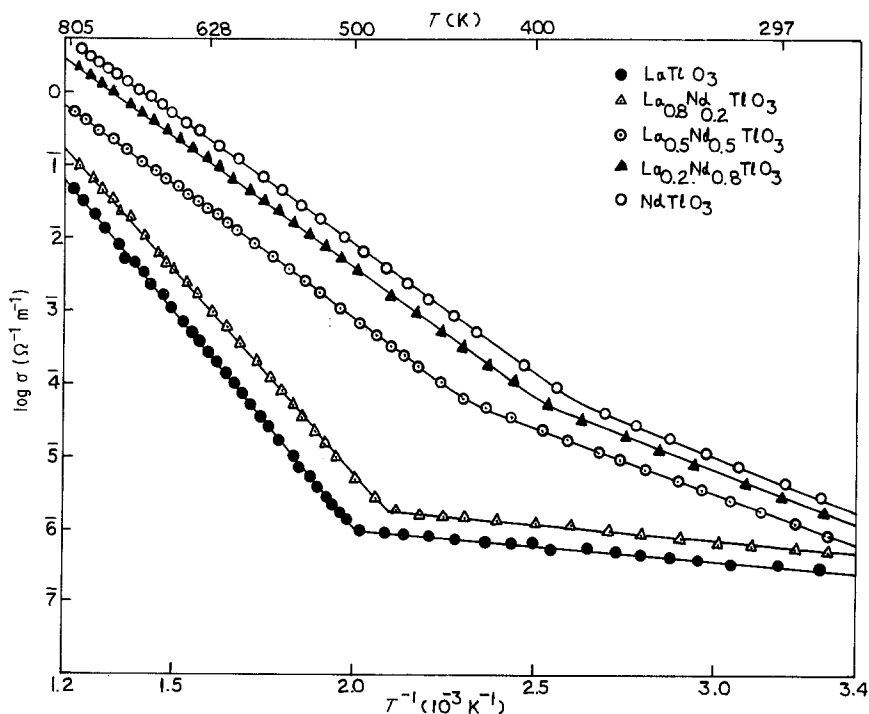


Figure 2 Variation of  $\log \sigma$  ( $\Omega^{-1} \text{m}^{-1}$ ) with inverse absolute temperature for the  $\text{La}_{1-x}\text{Nd}_x\text{TlO}_3$  system.

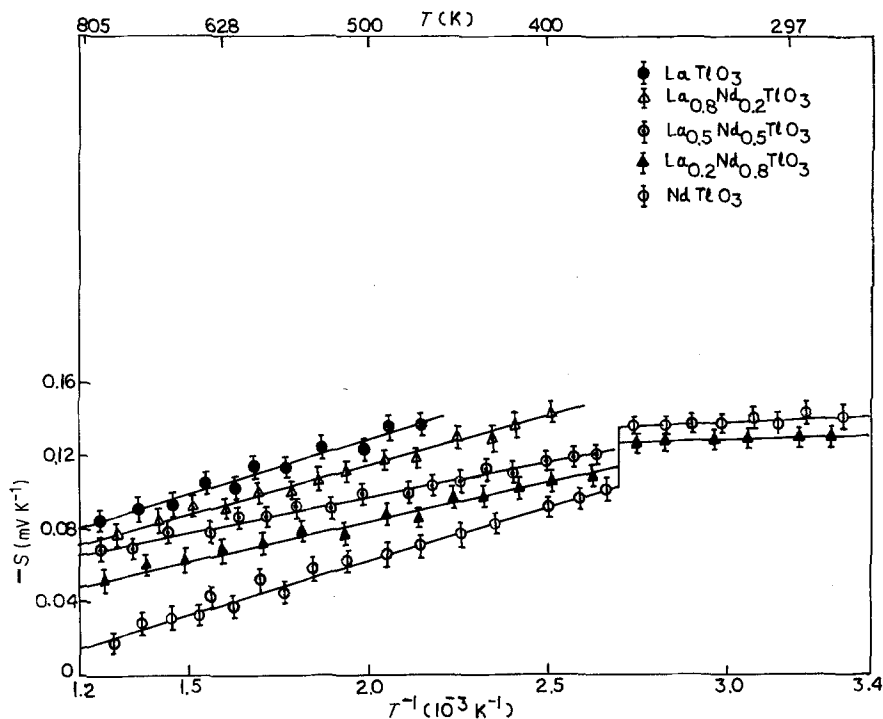


Figure 3 Variation of thermoelectric power,  $S$  ( $\text{mV K}^{-1}$ ) with inverse absolute temperature for  $\text{La}_{1-x}\text{Nd}_x\text{TiO}_3$ .

experimental points are in accordance with Equation 4. It is seen from this figure that plots of  $\log \sigma$  against  $T^{-1}$  are linear in all cases with breaks in the slope at specific temperatures ( $T_B$ ) which may be termed the break temperatures.

The Seebeck coefficient,  $S$ , at a particular temperature for all mixed metal thallates, is essentially independent of thermal history and life of the pellet, and is reproducible to  $\pm 5\%$ . Plots of  $S$  against  $T^{-1}$  are shown in Fig. 3. The sign of  $S$  is negative in all cases over the entire temperature range indicating that the charge carriers are electrons. Plots of  $S$  against  $T^{-1}$  also have two regions for only two mixed thallates, with break temperatures ( $T'_B$ ). The variation can be represented by the general equation

$$S = \frac{Q}{eT} + H. \quad (5)$$

The values of  $Q$  and  $H$  for different systems are given in Table II.

#### 4. Discussion

Plots of  $\log \sigma$  against  $T^{-1}$  have two linear regions; one at a temperature greater than  $T_B$  and another below  $T_B$ . The activation energy corresponding to the higher temperature is larger compared to that at lower temperature. The thermoelectric power (plots of  $S$  against  $T^{-1}$ ) were measured below  $T'_B$  only in the case of compounds with  $x = 0.8$  and  $1.0$ , and in other cases it was not measured due to the lower conductivity of the sample. In these cases  $S$  remains practically constant from  $300\text{ K}$  to  $T_B$ . This indicates that charge carriers are constant and are not thermally generated. Thus charge carriers are localized on defect centres, whose number is independent of temperature at least up to  $T_B$ . The conduction mechanism

TABLE II Summarized results of thermoelectric power for  $\text{La}_{1-x}\text{Nd}_x\text{TiO}_3$  ( $0.0 \leq x \leq 1.0$ ) systems

$x$	$Q$ (eV) ( $T < T'_B$ )	$H$ ( $\text{mV K}^{-1}$ ) ( $T < T'_B$ )	$T'_B$ (K)	$Q$ (eV) ( $T > T'_B$ )	$H$ ( $\text{mV K}^{-1}$ ) ( $T > T'_B$ )
0.0	—	—	—	0.060	+ 0.005
0.2	—	—	—	0.055	+ 0.005
0.5	—	—	370	0.052	— 0.022
0.8	0.004	0.115	370	0.430	— 0.060
1.0	0.010	0.110	370	0.040	— 0.020

TABLE III Summarized results of electrical conductivity for  $\text{La}_{1-x}\text{Nd}_x\text{TlO}_3$  ( $0.0 \leq x \leq 1.0$ ) systems

Parameters	System				
	$x = 0.0$	$x = 0.2$	$x = 0.5$	$x = 0.8$	$x = 1.0$
$\sigma_0(T)$ ( $T < T_B$ ) ( $\text{K } \Omega^{-1} \text{ m}^{-1}$ )	$3.89 \times 10^{-7}$	$7.24 \times 10^{-7}$	$4.17 \times 10^{-6}$	$1.22 \times 10^{-5}$	$1.62 \times 10^{-5}$
$E$ ( $T < T_B$ ) (eV)	0.08	0.10	0.27	0.37	0.39
$T_B$ (K)	485	455	425	390	378
$\sigma_0(T)$ ( $T > T_B$ ) ( $\text{K } \Omega^{-1} \text{ m}^{-1}$ )	19.95	31.62	22.39	56.23	79.43
$E$ ( $T > T_B$ ) (eV)	1.20	1.15	0.70	0.68	0.66
$E_g$ (eV)	2.40	2.30	1.40	1.36	1.32

in such a situation is the hopping type. The starting materials in the preparation of these compounds were relatively pure and hence we did not expect large chemical impurities in the systems. However, since these compounds were prepared by solid state reaction, a small amount of oxygen deficiency could not be ruled out. Each oxygen escape leaves two electrons within the crystal to preserve charge neutrality. These electrons left in the crystal may be trapped either in an oxygen ion vacancy or may be attached to cations. In the former case they will form donor centres and in the latter case  $\text{Tl}^{3+}:e$  centres. Formation of  $\text{La}^{3+}:e$  or  $\text{Nd}^{3+}:e$  is not expected as these ions do not have a multi-valency tendency. Donor centres are ionized on increasing the temperatures and conduct by a band mechanism. However, in these cases the slope of the  $\log \sigma$  against  $T^{-1}$  and  $S$  against  $T^{-1}$  plots are expected to be the same. This has not been found experimentally true. Thus, the presence of  $\text{Tl}^{2+}$  defect centres in these compounds seems more probable and conduction takes place owing to jumping of electrons from  $\text{Tl}^{2+}$  defect centre to  $\text{Tl}^{3+}$  normal sites. The activation energy for these systems increases from a compound with  $x = 0.0$  to one with  $x = 1.0$ .

At higher temperatures ( $T > T_B$ ) conduction is expected to be intrinsic and the dominant conduction mechanism is expected to be band type. The small value of  $S$  and its relatively low slope indicate that conduction may be due to both holes in the valence band and electrons in the conduction band. However, the dominant charge carriers are electrons as indicated by the sign of the charge carriers. The expression for conductivity for band conduction is given by the expression

$$\sigma = \sigma_0(T) \exp -\frac{E_g}{2kT}, \quad (6)$$

where  $\sigma_0(T)$  is a constant with a very small tem-

perature variation, and  $E_g$  is the band gap of the solid. The values of  $\sigma_0(T)$  and  $E_g$  obtained are given in Table III. As is evident from this table,  $E_g$  decreases as  $x$  increases. For pure  $\text{LaTlO}_3$  the band gap is 2.40 eV and for  $\text{NdTlO}_3$  it is 1.32 eV. For other compounds it lies between these values.

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