

Electrical conduction in the solid solution

$\text{La}_{1-x}\text{Na}_x\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ ($0.01 \leq x \leq 0.99$)

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Abstract. Seebeck coefficient and DC resistivity of the solid solution $\text{La}_{1-x}\text{Na}_x\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ ($0.01 \leq x \leq 0.99$) have been measured in the temperature range 300–900 K. Seebeck coefficient is positive for all compositions over the temperature range of measurements. Conduction is due to $3d$ electrons of cobalt ions in the compositions with $x \leq 0.60$. Conduction occurs among localized sites for compositions with $x \geq 0.70$.

Keywords. Lanthanum cobaltate; sodium niobate; lanthanum sodium cobalt niobium oxide.

1. Introduction

Electrical behaviour of lanthanum cobaltate LaCoO_3 modified by substituting Ca^{2+} , Sr^{2+} or Ba^{2+} at La^{3+} (A) site (Raccah and Goodenough 1968; Bhide *et al* 1975; Rao *et al* 1975a, 1977; Obayashi *et al* 1976; Patil *et al* 1979) or Fe^{3+} , Ni^{3+} , Ti^{4+} etc. at Co^{3+} (B) site (Rao *et al* 1975b; Parkash 1978; Bahadur and Parkash 1983; Kumar *et al* 1985) has been investigated extensively in the last two decades. Substitution of alkaline earth ions i.e. Ca^{2+} , Sr^{2+} or Ba^{2+} for La^{3+} in LaCoO_3 generates tetravalent cobalt ions in order to maintain electrical charge neutrality. Simultaneous presence of Co^{3+} and Co^{4+} ions enhances their electrical conductivity and the systems exhibit metallic behaviour above a critical concentration. For Fe^{3+} and Ni^{3+} substituted LaCoO_3 , the properties change systematically with substituent concentration (Rao *et al* 1975b; Parkash 1978). In Ti^{4+} substituted LaCoO_3 , the electrical resistivity increase with increasing Ti^{4+} concentration due to breaking of Co-O-Co links responsible for conduction (Bahadur and Parkash 1983).

The effect of compensated valence substitutions at A and B sites on the electrical behaviour of LaCoO_3 has not been studied much. We have in recent years investigated the possibility of the formation of such solid solutions e.g. $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-x}\text{Ti}_x\text{O}_3$ (Bahadur and Parkash 1983) and $\text{La}_{1-x}\text{Pb}_x\text{Co}_{1-x}\text{Ti}_x\text{O}_3$ (Parkash *et al* 1987; Kumar *et al* 1987) and studied their electrical behaviour. It has been found that independent substitutions at A or B site has limited solid solubility determined by the difference in the ionic radii and valency of the substituents and the ions to be substituted. However, solid solution is formed over the entire range of compositions in the above compensated systems. Recently we have reported the formation of solid solution in the system $\text{La}_{1-x}\text{Na}_x\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ for all values of x between 0 and 1 as well as the crystal structure of various compositions in it (Parkash *et al* 1988). In this paper we report their electrical behaviour.

2. Experimental

All the samples were prepared by the ceramic method using lanthanum oxalate,

cobalt oxalate, sodium carbonate and niobium pentaoxide, all having a purity of 99.9% or better. The preparation details were reported earlier (Parkash *et al* 1988). Formation of single phase materials was confirmed by X-ray diffraction. The samples were chemically analysed by atomic absorption spectrophotometer (Perkin Elmer). Resistivity was measured on sintered cylindrical pellets by two-probe or four-probe methods depending on whether the resistance was high or low respectively. The samples were coated with Au-Pd alloy by evaporation for two probe DC resistivity measurements. The resistance was measured by an electrometer (Keithley 616). The Seebeck coefficient α was measured relative to platinum in the temperature range 350–800 K.

3. Results and discussion

All the samples were single phase materials as indicated by their X-ray diffraction data. The crystal structure is rhombohedral (R) for samples with $x \leq 0.30$ similar to LaCoO_3 and cubic (C) in the range $x = 0.40$ – 0.95 . The composition with $x = 0.99$ is orthorhombic (O) similar to NaNbO_3 (Parkash *et al* 1988). It is worth mentioning that though the overall symmetry is cubic for samples with x in the range 0.40 – 0.95 , the presence of asymmetry and very slight splitting in the higher angle X-ray diffraction lines indicate slight distortion from the cubic symmetry in the compositions with $x \geq 0.50$. Similar results have been reported in the systems, lanthanum lead zirconate titanate (Wolters and Burgraaf 1974) and lanthanum lead cobalt titanate (Kumar *et al* 1987). Chemical analysis of sodium and cobalt in the various samples indicates that the samples are stoichiometric in accordance with the formula $\text{La}_{1-x}\text{Na}_x\text{Co}_{1-x}\text{Nb}_x\text{O}_3$. This shows that cobalt and niobium ions are mostly in the trivalent and pentavalent states respectively. However, the possibility of the presence of small amounts of divalent cobalt ions is not ruled out in view of the slight oxygen deficiency due to higher firing temperatures (Menyuk *et al* 1967).

The Seebeck coefficient, α , is positive for all samples with $x \leq 0.60$ over the entire range of measurements. This shows that holes are the majority charge carriers. Typical plots of α vs T for a few compositions are shown in figure 1. The value of α remains almost independent of temperature within experimental error for samples with $x = 0.10$ and 0.20 while it shows slight increase with temperature for samples with $x = 0.30$ – 0.60 . Values of α at 500 K for all the above compositions are given in table 1. Plots of $\log \rho_{\text{DC}}$ vs $1000/T$ for samples with x in the range 0.01 – 0.60 and 0.70 – 0.99 are given in figures 2 and 3 respectively. Plots for the compositions with $x = 0.30$, 0.50 and 0.80 are omitted to maintain clarity of the figures. The plots for these compositions are close to those of $x = 0.40$, 0.60 and 0.90 respectively. Two or more different temperature regions are observed in all these plots. The behaviour in each region can be described by an Arrhenius type relation $\rho = \rho_0 \exp(E/kT)$ where E is the activation energy for conduction. The temperature regions and the corresponding activation energies are given in table 1.

Electron transport properties of LaCoO_3 were reported earlier (Bhide *et al* 1972). It is a p -type semiconductor in which low-spin Co^{III} ions transform to high spin Co^{3+} ions upto 200K. Activation energy in this region is 0.1 eV. Between 200 and 400 K, electron transfer occurs between Co^{III} and Co^{3+} ions generating intermediate charge transfer states Co^{2+} , Co^{IV} etc. Activation energy of conduction in this region is 0.2 eV (region I) which represents the gap between the filled t_{2g}^6 orbitals and empty σ^*

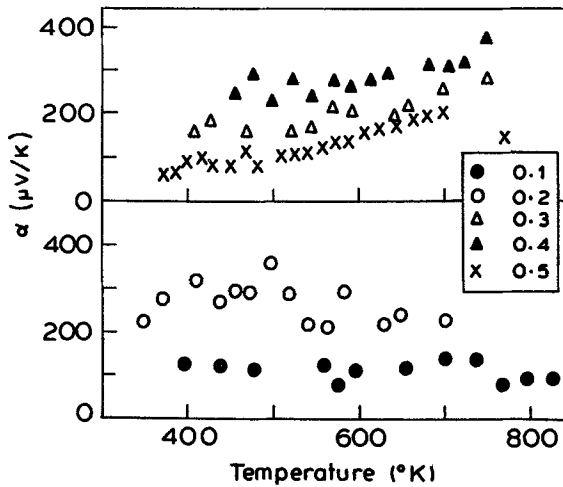


Figure 1. Variation of Seebeck coefficient, α , with temperature for $\text{La}_{1-x}\text{Na}_x\text{Co}_{1-x}\text{Nb}_x\text{O}_3$.

Table 1. Structure, Seebeck coefficient α and activation energy E in different temperature regions.

Composition x	Structure	α $\mu\text{V/K}$	Region I		Region II		Region III	
			(K)	E (eV)	(K)	E (eV)	(K)	E (eV)
0.01	R	—	300–375	0.17	375–525	0.43	—	—
0.05	R	50	300–400	0.19	400–525	0.25	—	—
0.10	R	110	—	—	300–520	0.24	535–850	—
0.20	R	360	—	—	300–450	0.29	450–650	—
0.30	R	110	—	—	300–450	0.34	450–650	—
0.40	C	220	300–370	0.23	370–500	0.33	525–750	—
0.50	C	110	—	—	325–450	0.44	450–600	—
0.60	C	120	—	—	310–500	0.40	500–675	—
0.70	C	—	300–400	0.40	400–650	0.54	> 650	0.42
0.80	C	—	320–520	0.37	520–700	0.61	> 700	0.40
0.90	C	—	300–390	0.26	390–670	0.56	> 670	0.02
0.95	C	—	300–480	0.27	480–700	0.64	> 700	0.16
0.99	O	—	350–480	0.10	480–650	0.59	> 800	—
					650–800	1.42		

band formed from e_g orbitals. Between 400 and 650 K, short range ordering of low-spin and high-spin ions occur leading to a sharp decrease in the resistivity with an activation energy of 0.54 (region II). Beyond 650 K, resistivity changes slightly indicating saturation of charge carriers (region III) and finally it undergoes a first order transition from localized to collective behaviour of d -electrons. Both electrons and holes contribute to conduction in LaCoO_3 . The electrons are present in orbitals of e_g symmetry and holes in orbitals of t_{2g} symmetry. Their total numbers (trapped plus mobile) are equal. The p -type character of LaCoO_3 in the temperature range 300–1200 K shows that the mobility of holes is greater than that of electrons.

The behaviour of electrical resistivity of the samples in the range $x=0.01$ – 0.60 is essentially similar to that of LaCoO_3 . The resistivity increases with x . This indicates that conduction is mainly due to 3d-electrons of cobalt ions. Region I of LaCoO_3 is

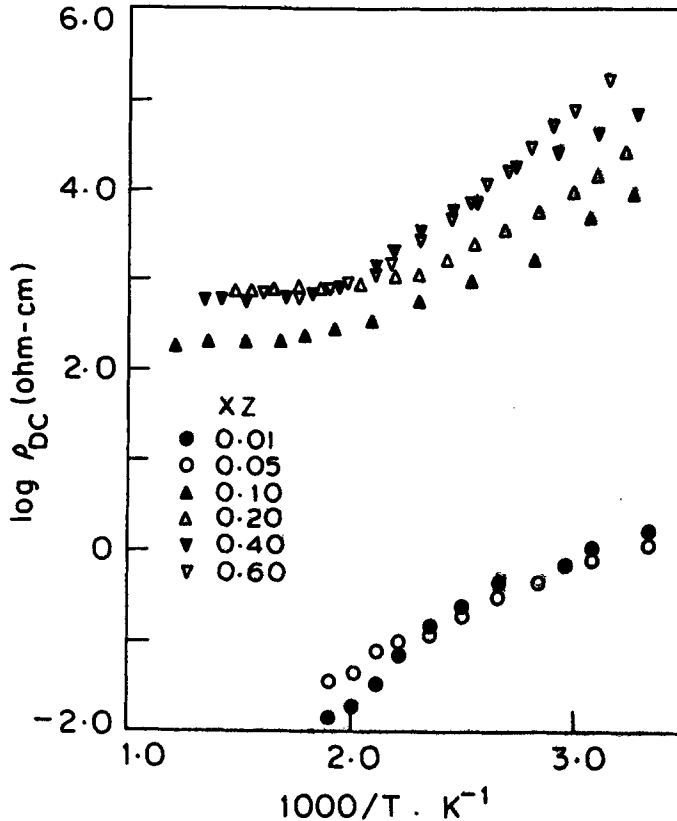


Figure 2. Plots of $\log \rho_{DC}$ vs $1000/T$ for $\text{La}_{1-x}\text{Na}_x\text{Co}_{1-x}\text{Nb}_x\text{O}_3$.

clearly seen in the samples with $x=0.01$ and 0.05 . In other samples this region appears to occur below 300 K. This may be due to the change in the relative values of crystal field splitting, Δ_{cf} and exchange energy, Δ_{ex} with composition. Region II of LaCoO_3 is clearly seen in all these samples. The activation energies are in the range 0.25–0.45 eV. This region is followed by a region III of almost temperature independent resistivity indicating saturation of charge carriers. Slight increase of α with temperature in the samples with $x=0.20$ – 0.60 may be due to the presence of small amount of divalent cobalt ions which act as donors. These donor states get exhausted with increasing temperature leading to an increase in α with temperature. Hopping of the charge carriers between Co^{2+} and Co^{3+} may also contribute to the total observed conductivity. This is supported by results of frequency dependence of AC conductivity of these samples (to be published later).

The resistivity behaviour of all the samples with $x \geq 0.70$ is similar. The resistivity changes by about four orders of magnitude in going from $x=0.60$ to $x=0.70$. The break in the $\log \rho_{DC}$ vs $1000/T$ plot of $x=0.99$ which occurs near 650 K is quite close to the anti-ferroelectric-paraelectric transition temperature (628 K) of NaNbO_3 (Jaffe *et al* 1971). The resistivity drops very sharply after this temperature. The activation energy of conduction in region II of all the samples is about the same. This shows that the same conduction mechanism is operative in all these samples.

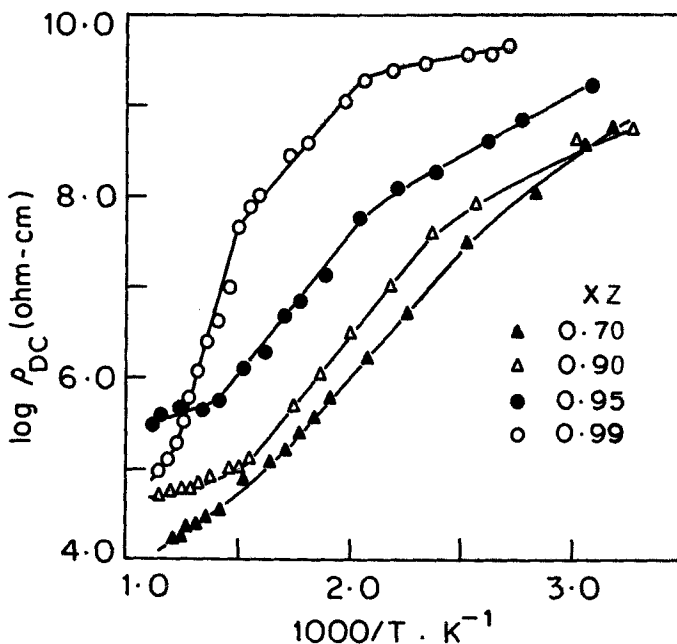


Figure 3. Plots of $\log \rho_{DC}$ vs $1000/T$ for $\text{La}_{1-x}\text{Na}_x\text{Co}_{1-x}\text{Nb}_x\text{O}_3$.

The observed resistivity behaviour of $\text{La}_{1-x}\text{Na}_x\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ can be summarized as follows: compositions with $x=0.01$ and 0.05 behave similar to LaCoO_3 ; Nb^{5+} and Na^+ ions basically act as scattering centres. The conduction in this system is due to Co-O-Co links, which decreases with increasing x . Impurity conduction occurs among localized sites due to cobalt ions in the composition with $x \geq 0.70$. In these compositions, the concentration of cobalt ions may not be sufficient to form impurity band. The absence of the systematic increase of resistivity with x in this system shows that it is highly structure-sensitive.

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