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Electrical and magnetic properties of the system $LaNi_{1-x}Fe_xO_3$

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Abstract. Electrical and magnetic properties of the system $LaNi_{1-x}Fe_xO_3$ ($0<x\leq0{\cdot}3$) have been investigated. The system shows metallic behaviour similar to $LaNiO_3$ upto $x=0{\cdot}1$ while the sample with $x=0{\cdot}3$ shows semiconducting behaviour. Oxygen partial pressure dependence of electrical resistivity is noticed in the composition $LaNi_{0{\cdot}9}Fe_{0{\cdot}1}O_3$.

Keywords. Spin state equilibrium; perovskite oxides; electrical resistivity; Seebeck coefficient; lanthanum nickelate, lanthanum ferrite.

1. Introduction

Transition metal oxide perovskites of the type ABO_3 where A is a rare earth ion and B is a transition metal ion have attracted considerable attention in recent years because of their interesting electrical and magnetic properties (Goodenough 1963, 1966, 1967, 1972, 1974; Frederikse 1970; Rao and Subbarao 1970; Rao 1974; Subbarao *et al* 1971) as well as potential applications as components of solid electrolyte fuel cells (Tedmon *et al* 1969), as cathode materials in alkaline solution zinc air batteries (Meadowcraft 1970; Kudo *et al* 1975) (used in urban transport) and as active catalysts for the oxidation of carbon monoxide in auto-exhaust gases (Libby 1971; Voorhoeve *et al* 1972; Om Parkash *et al* 1974) and so on. Electronic and magnetic properties of these materials are largely determined by the spin state S, of the transition metal ion and this aspect has been discussed in detail in the literature (Goodenough 1967; 1974; Rao and Subbarao 1970, Rao 1974). Accordingly, $LaNiO_3$ with low spin Ni^{3+} in $S=\frac{1}{2}$ state is Pauli-paramagnetic metal due to the presence of itinerant-d-electrons while $LaFeO_3$ with high-spin Fe^{3+} in the $S=5/2$ state is an anti-ferromagnetic insulator due to presence of localized d-electrons. $LaCoO_3$ with Co^{3+} in the low ($S=0$) or the high ($S=2$) spin states exhibits localized or itinerant properties of d-electrons depending on the conditions. Recently, we reported results of our studies (Rao *et al* 1975) on $LaNi_{1-x}Co_xO_3$ and $LaCO_{1-x}Fe_xO_3$ over a wide range of compositions and these studies clearly showed the interplay of localized versus itinerant behaviour of d-electrons in these systems. Thus, $LaNi_{1-x}Co_xO_3$ with $x\leqslant0{\cdot}5$ shows itinerant electron behaviour while compositions with $x>0{\cdot}5$ show behaviour of localized electrons. We considered it interesting to investigate the electronic and magnetic properties of the system $LaNi_{1-x}Fe_xO_3$ wherein a high-spin ion (Fe^{3+}) is incorporated into metallic $LaNiO_3$ containing low-spin Ni^{3+}.

Our interest in the $LaNi_{1-x}Fe_xO_3$ system was further strengthened by the possibility of using these materials as interconnection materials in fuel cells. Interconnection materials must satisfy the following criteria: (a) they must be stable both in air and fuel atmospheres, (b) they should be good electronic conductors, (c) they should not react with other components of the battery, (d) they should not contain pores. Kleinschmager and Reich (1972) have reported that the electrical resistivity of the system, $LaO_{1.5}|NiO_{1.5}|CoO_{1.33}$ ($\equiv$10 9 1) varies only marginally with oxygen partial pressure. This composition of Kleinschmager and Reich (1972) roughly corresponds to $LaNi_{0.9}\,Co_{0.1}\,O_3$. It was, therefore, considered worthwhile to actually prepare the solid solution in the related system $LaNi_{1-x}Fe_xO_3$ and investigate its electronic properties.

2. Experimental

The members of the system $LaNi_{1-x}Fe_xO_3$ were prepared using lanthanum oxalate, nickel oxalate and ferric oxide (all of better than 99·99% purity) as starting materials. Stoichiometric quantities of these materials were mixed and the mixtures decomposed by heating slowly in air up to 975 K. The resulting mixtures were dissolved in aqua-regia and the solutions evaporated to dryness. The solid residue was dissolved in water and this solution was dripped very slowly into a large excess of concentrated sodium carbonate solution under constant stirring. The precipitate was filtered and washed with water a number of times. The precipitate was dried and heated slowly in air at 1075 K. The resulting material was digested with hot water a number of times to remove Na^+ ions. It was then dried, pelletized and fired at 1175 K in an oxygen atmosphere for 24–48 hr. Compound formation was confirmed by recording x-ray diffraction patterns using a GE XRD-5 diffractometer.

TGA was recorded using MOM derivatograph at a heating rate of 10°/min. Resistivity measurements were made on thick sintered pellets employing the four-probe technique. Seebeck coefficients were measured relative to platinum using a set-up fabricated locally. Magnetic susceptibility measurements were carried out employing a Gouy balance.

3. Results and discussion

All the samples studied were found to have rhombohedral structure. The lattice parameters of the system $LaNi_{1-x}Fe_xO_3$ are listed in table 1. We see that a_R and α_R are

Table 1. Lattice parameters of $LaNi_{1-x}Fe_xO_3$

$LaNi_{1-x}Fe_xO_3$ x	a_R, A°	α_R°
0	5·41	60·69
0·01	5·43	60·62
0·05	5·44	60·55
0·10	5·40	60·73
0·30	5·48	60·94

nearly constant. This is probably because Ni^{3+} and Fe^{3+} have nearly equal ionic radii.

Plots of the logarithm of electrical resistivity ($\log \rho$) against the reciprocal of absolute temperature for the $LaNi_{1-x}Fe_xO_3$ ($0{\cdot}0 < x \leqslant 0{\cdot}3$) system are shown in figure 1. The results clearly show that incorporation of the high-spin Fe^{3+} ions into $LaNiO_3$ has more drastic effects than the incorporation of Co^{3+} ions into $LaNiO_3$. $LaNi_{1-x}Fe_xO_3$ remains metallic only up to $x \approx 0{\cdot}1$ while $LaNi_{1-x}Co_xO_3$ exhibits metallic behaviour up to $x = 0{\cdot}5$ (Rao *et al* 1975). When $x = 0{\cdot}3$, $LaNi_{1-x}Fe_xO_3$ becomes semiconducting although the temperature dependence of resistivity is not very significant. The resistivity behaviour of this sample ($x = 0{\cdot}3$) is interesting, the resistivity is essentially temperature independent at low temperatures and decreases only slightly at higher temperatures.

Seebeck coefficients of $LaNi_{1-x}Fe_xO_3$ are plotted against temperature in figure 2. Consistent with the resistivity data, the material behaves like the parent $LaNiO_3$ when $x < 0{\cdot}3$ over the entire temperature range of 400–1000 K (with n-type behaviour). However, the composition with $x = 0{\cdot}3$ shows a distinct increase in Seebeck coefficient with increase in temperature at higher temperatures. Increase of α with T in this

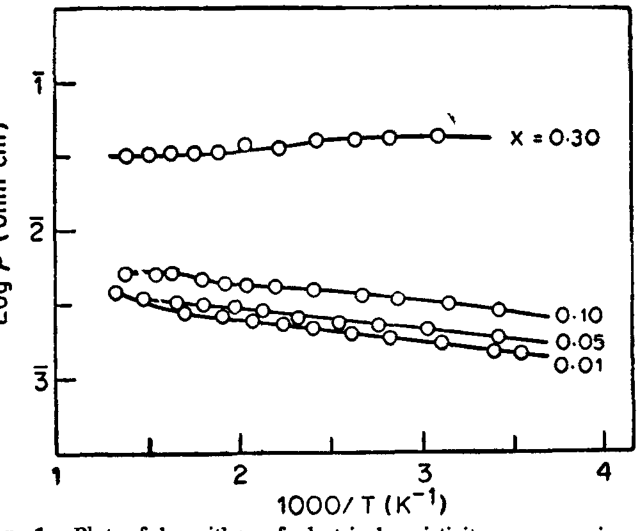

Figure 1. Plot of logarithm of electrical resistivity versus reciprocal of absolute temperature for $LaNi_{1-x}Fe_xO_3$.

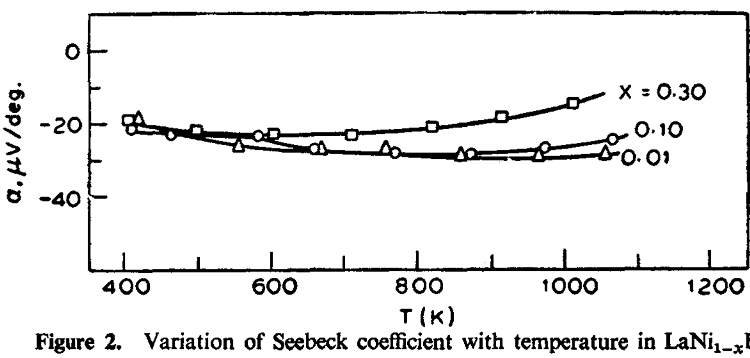

Figure 2. Variation of Seebeck coefficient with temperature in $LaNi_{1-x}Fe_xO_3$.

sample is suggestive of an electron hopping mechanism operating at higher temperature in this sample.

Magnetic susceptibility data $LaNi_{1-x}Fe_xO_3$ have been analysed in terms of plot χT versus temperature as shown in figure 3. Such χT-T plots are known to reflect variation of spin state population in such a system (Rao *et al* 1975). When $x<0{\cdot}3$, the plots are linear with positive slopes just as in the case of $LaNi_{1-x}Co_xO_3$ ($x<0{\cdot}5$). $LaNi_{1-x}Fe_xO_3$ with $x=0{\cdot}3$, shows an increasing trend of χT with increase in temperature (with a slope similar to samples with $x<0{\cdot}3$), but χT seems to approcah a

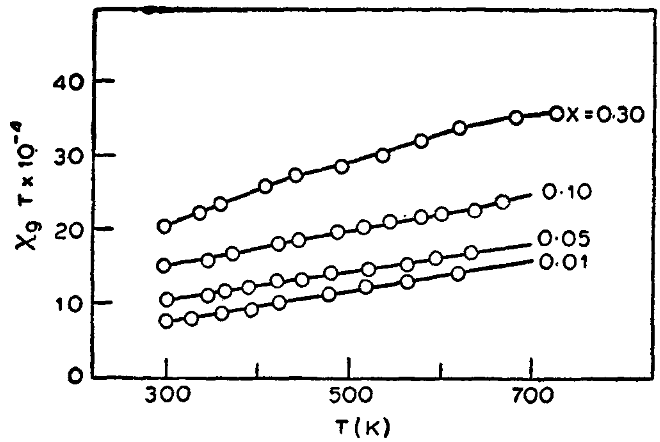

Figure 3. Variation of χT with temperature in $LaNi_{1-x}Fe_xO_3$.

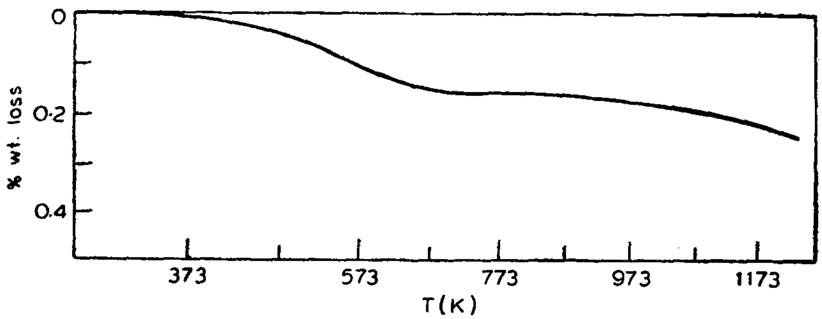

Figure 4. TGA curve of $LaNi_{0{\cdot}9}Fe_{0{\cdot}1}O_3$.

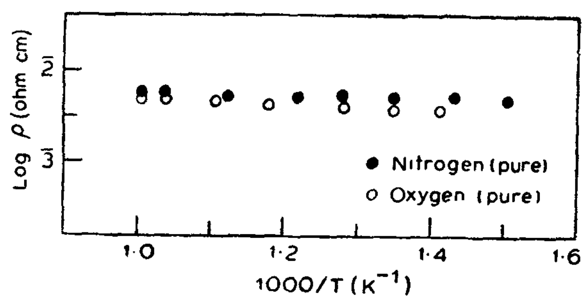

Figure 5. Plot of logarithm of electrical resistivity against reciprocal of absolute temperature for $LaNi_{0{\cdot}9}Fe_{0{\cdot}1}O_3$.

constant value at high temperatures, a behaviour typical of simple paramagnetic materials. Samples of $LaNi_{1-x}Fe_xO_3$ ($x>0·3$) showed field-dependent magnetic susceptibility similar to $LaFeO_3$ and we, therefore, did not pursue studies on these samples.

$LaNiO_3$ loses oxygen in well defined equilibrium stages (Gai and Rao 1975; Obayashi and Kudo 1975). At 1390 K $LaNiO_3$ decomposes to La_2NiO_4 and NiO; slightly below this temperature (1210 K), $LaNiO_3$ seems to undergo a rhombohedral-cubic transition. Consistent with the oxygen loss, the electrical resistivity of $LaNiO_3$ varies with oxygen partial pressure (Obayashi and Kudo 1975). The TGA curve of the sample $LaNi_{0.9}Fe_{0.1}O_3$ shown in figure 4 indicates that with the incorporation of iron in $LaNiO_3$, oxygen loss (with the increase in temperature) is reduced considerably. We have measured the electrical resistivity of $LaNi_{0.9}Fe_{0.1}O_3$ in the range of 600–1000 K in atmospheres of pure nitrogen ($p_{O_2} < 10^{-6}$ atm.) and pure oxygen. The results are shown in figure 5. The results indicate that there is some oxygen partial pressure dependence of resistivity in this system. Therefore, $LaNi_{0.9}Fe_{0.1}O_3$ may not be a good candidate for interconnection materials in fuel cells.

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