

LaNi_{1-x}Co_xO₃ as interconnection materials

OM PARKASH

Advanced Centre for Materials Science, Indian Institute of Technology,
Kanpur 208 016

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Abstract. Thermo Gravimetric Analysis (TGA) shows that incorporation of Co²⁺ considerably reduces the oxygen loss at high temperatures in LaNiO₃. Electrical resistivity of LaNi_{1-x}Co_xO₃ ($x \leq 0.2$) is essentially independent of oxygen partial pressure in the 600-1000 K range.

1. Introduction

Rare earth perovskites of the type ABO₃ where A is a rare earth ion and B is a transition metal ion have been found to have potential applications such as components of solid electrolyte fuel cells (Tedmon *et al* 1969) and as cathode materials in alkaline solution zinc-air batteries (Meadowcraft 1970; Kudo *et al* 1975) (used in urban transport). Electrical and magnetic properties of these materials have been investigated extensively in recent years (Goodenough 1967, 1972, 1974; Rao 1974, 1977; Rao and Subba Rao 1970). We have been actively involved in the investigation of solid solutions of perovskites such as LaNi_{1-x}Fe_xO₃ and LaNi_{1-x}Co_xO₃ in this laboratory for quite some time and we recently reported electronic and magnetic properties of LaNi_{1-x}Co_xO₃ ($0 \leq x \leq 1$) and LaCo_{1-x}Fe_xO₃ ($0 \leq x \leq 0.5$) (Rao *et al* 1975). Our interest in the study of these materials was further strengthened because of their possible use as interconnecting materials in fuel cells. Interconnection materials must be stable both in air and fuel atmospheres (i.e., should have conductivity independent of oxygen partial pressure, etc.) and should be good electronic conductors. Kleinschmager and Reich (1972) have reported that the electrical resistivity of the system LaO_{1.5} | NiO_{1.5} | CoO_{1.33} (10|9|1) varies marginally with oxygen partial pressure. This composition roughly corresponds to LaNi_{0.9}Co_{0.1}O₃. It was, therefore, considered worthwhile to actually prepare solid solutions of finite compositions in the system LaNi_{1-x}Co_xO₃ and study their electrical properties.

2. Experimental

Samples of LaNi_{1-x}Co_xO₃, $x = 0.1$ and 0.2 , were prepared by mixed oxalate method (Rao *et al* 1975). They have rhombohedral structure with $a = 5.41 \text{ \AA}$, $\alpha = 60.69^\circ$ and $a = 5.40 \text{ \AA}$ and $\alpha = 60.76^\circ$ respectively. TGA was carried out,

using MOM-505 Derivatograph at a heating rate of $10^\circ/\text{min}$. Resistivity measurements were carried out employing four-probe technique using a locally fabricated cell. For a particular atmosphere, the conductivity cell was placed in a quartz jacket and the entire system was evacuated to a pressure less than one micron. The system was then flushed with the required gas and the entire system again evacuated. This process of flushing and evacuation was repeated a number of times and finally the atmosphere of the required gas was maintained in the closed system.

3. Results and discussion

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. TGA curves of the samples of $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.1$ and $x = 0.2$) are shown in figure 1. We see that incorporation of Co^{3+} in LaNiO_3 reduces the oxygen loss considerably thus indicating the relative stability of these materials compared to pure LaNiO_3 .

Resistivity data for the system $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.1$ and $x = 0.2$) are shown in figure 2. The resistivity of $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.1$ or $x = 0.2$) is essentially

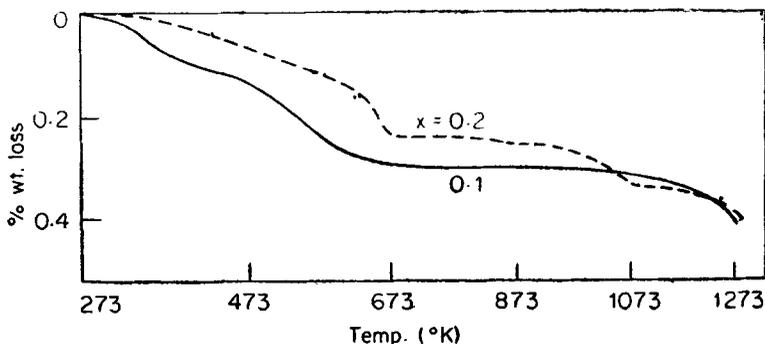


Figure 1. TGA curves of $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$.

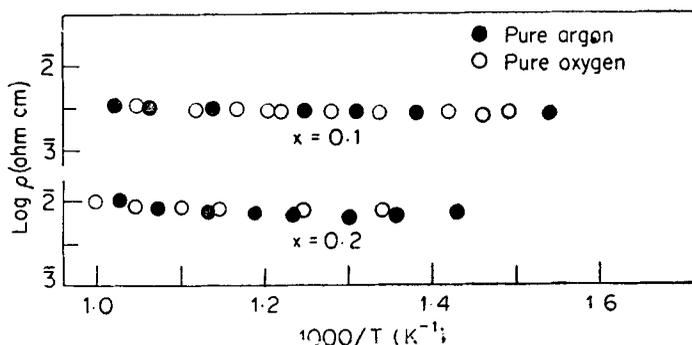


Figure 2. Plot of logarithm of electrical resistivity of $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$ [against reciprocal of absolute temperature].

independent of oxygen partial pressure over the entire range of measurement (600–1000 K). It, therefore, appears that $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.1-0.2$) is a suitable candidate for use as interconnection material. $\text{LaNi}_{0.9}\text{Fe}_{0.1}\text{O}_3$, on the other hand, does not appear to be so since the resistivity varies appreciably with oxygen partial pressure. Actual use of $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$ in fuel cells, however, requires that the material be essentially inert and non-porous and these studies have yet to be carried out.

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