STRUCTURAL AND ELECTRICAL PROPERTIES OF $\text{LaCo}_{1-x}\text{Ni}_x\text{O}_3$

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We investigated the effect of Ni doping on the structural and electrical properties of LaCoO_3 . Single phase $\text{LaCo}_{1-x}\text{Ni}_x\text{O}_3$ ($x = 0, 0.1, 0.3, 0.5$) were synthesized using solid state reaction method. Space group, lattice constants and atomic positions were determined by Rietveld refinement of powder diffraction data. The unit cell parameters found to increase with Ni doping. Four-probe direct current conductivity measurements were also carried out to investigate transport behavior of compounds. Samples were found to exhibit temperature dependent semiconducting behavior. The drastic improvement of the room-temperature conductivity of doped samples with respect to the pure compound has been observed and explained in terms of decrease in band gap. The transport mechanism in different regions of temperature has been investigated by fitting Arrhenius and variable range hopping (VRH) models.

Keywords: XRD, Rietveld, Resistivity, VRH.

1. Introduction

Rare earth cobaltites are interesting ceramic material for study and controversially debated for last five decades, (see review Ref.1). Due to the possibility of inducing and controlling spin-state transition of Co ion through chemical substitution, temperature, or external pressure the study of doped cobaltites has become quite interesting. The effect of such doping in many such cobaltites has already been investigated and alkaline-earth-doped LaCoO_3 and NdCoO_3 are extensively used as catalysts, sensors and thermoelectric materials.^{2, 3} In the present study we have investigated the effect of Ni doping on the structural and electrical transport properties of LaCoO_3 .

2. Experimental Details

The single phase $\text{LaCo}_{1-x}\text{Ni}_x\text{O}_3$ ($x = 0, 0.1, 0.3, 0.5$) was prepared by conventional solid state reaction method. XRD measurements were performed using a high resolution Bruker D8 advanced x-ray diffractometer having $\text{Cu-K}\alpha$ source. For the dc-conductivity measurements of the samples, an automated resistance measuring set up; consisting a standard four-probe unit in temperature range 85 K- 300 K was used.

3. Results and Discussion

The Rietveld refined XRD patterns of samples are shown in Fig 1. A good fit was obtained and analysis at room temperature suggests that all the samples exhibit single phase with rhombohedral structure and $R\bar{3}c$ space group.

Fig. 1. Rietveld Refined XRD pattern of $\text{LaCo}_{1-x}\text{Ni}_x\text{O}_3$

In $\text{LaCo}_{1-x}\text{Ni}_x\text{O}_3$, La is associated with Wyckoff position $6a$ ($0, 0, 1/4$), Co is at position $6b$ ($0, 0, 0$), O is at $18e$ ($x, 0, 1/4$). The unit cell parameters increase with the nickel doping (see Table.1) and hence the volume also increases, which is consistent with the ionic radii differences and it implies that Co^{+3} is replaced by either Ni^{+2} or Ni^{+3} ($r(\text{Ni}^{+2}) > r(\text{Ni}^{+3}) > r(\text{Co}^{+3})$).⁴

Table 1. Reitveld refined unit cell parameters, activation energy (E_a) and localization length (ξ) for $\text{LaCo}_{1-x}\text{Ni}_x\text{O}_3$.

x	a (Å)	c (Å)	χ^2	E_a (eV)	$T_{0(ES)}$ $\times 10^3$ (K)
0	5.4441	13.097	1.38	0.12	142.9
0.1	5.4489	13.105	2.14	0.06	28
0.3	5.4605	13.122	2.15	-	12.09
0.5	5.4700	13.143	1.02	-	0.724

Fig. 1. Electrical resistivity Vs. Temperature

The dc conductivity measurements reveal that all samples exhibit temperature dependent semiconducting behavior in the measured range of temperature (Fig 2). From figure 3(b), it is clear that no single conduction mechanism can explain the transport behavior in the measured temperature range. The data have been fitted with various conduction models and found that for samples with $x = 0, 0.1$, conduction mechanism at high temperature region ($\sim 200\text{--}300\text{ K}$) is governed by Arrhenius law:

$$\rho = \rho_0 \exp(kT) \quad (1)$$

representing a thermally activated behavior due to the presence of gap E_a (thermal activation energy of electrical conduction) as seen in figure 3(a). The activation energy decreases with nickel doping (Table.1), which indicates the fact that band gap is decreasing with Ni doping because of increase in carrier concentration and hence there is decrease in resistivity. For samples with $x = 0, 0.1$, in low temperature region ($\sim 100\text{--}200\text{ K}$) a good fit was found with Efros–Shklovski (ES) variable range hopping law⁵:

Fig. 3(a). $\ln \rho$ Vs $1/T$, (b) $\ln \rho$ Vs $T^{-1/2}$

$$\rho = \rho_0 \exp(T_0 / T)^{\frac{1}{2}}. \quad (2)$$

$$T_{0(ES)} = 2.8e^2 / k\varepsilon\xi. \quad (3)$$

However for $x = 0.3, 0.5$ variable range hopping model fits well for full measured temperature range (85-300K), which suggests that nickel doping induces more disorder in the system and thus the conduction is governed by variable range hopping mechanism. From table 1 we found that $T_{0(ES)}$ which is calculated from the slope of $\ln \rho$ vs $T^{-1/2}$ decreases as Ni dopant concentration increases which suggests that localization length (ξ) increases and hence leads to the observed decrease in resistivity

4. Conclusion

We prepared $\text{LaCo}_{1-x}\text{Ni}_x\text{O}_3$ ($x = 0, 0.1, 0.3, 0.5$) ceramic samples using solid state reaction method. Single phase rhombohedral structure with $R\bar{3}c$ space group was confirmed from Reitveld refinement of XRD data. Unit cell parameters found to increase with doping, which is consistent with the differences in ionic radii of Co and Ni. Electrical resistivity found to decrease with doping which is attributed to increase in carrier concentration and decreasing band gap. Disorder induced ES variable range hopping mechanism for conduction found to dominant in doped samples and localization length increases with increase in Ni doping and hence leads to decrease in resistivity.

References

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