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Structural and Transport Studies on $LaAl_{1-x}Co_xO_3$

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Abstract. We report the structural and dc transport studies on $LaAl_{1-x}Co_xO_3$ (x = 0.2, 0.5, 0.8, 1.0). $LaAl_{1-x}Co_xO_3$ samples have been prepared by solid state reaction synthesis. P-XRD patterns refined using FullProf to get the unit cell dimensions and the Co-O bond lengths. The intermediate samples exhibited mixture of rhombohedral and monoclinic phase indicating the distorted nature. The low temperature DC transport reveals small polaron hopping conduction with increasing activation energies with decrease in Co concentration.

Keywords: Rietveld Refinement, DC resistivity, Small polaron.
PACS: 61.05.cp, 71.38.Ht

INTRODUCTION

$LaCoO_3$ has been a subject of intense research over the past few decades primarily because of the thermally excited spin state transition associated with the Co^{3+} ions which are octahedrally coordinated by O^{2-} in the prototypical perovskite structure (ABO_3)[1-7]. The delicate balance between the crystal field splitting energy (Δ_{CF}) and the Hund's coupling (Δ_{EX}) allows the Co^{3+} ions to adopt either a Low Spin (LS) ($t_{2g}^6 e_g^0$, S=0), Intermediate Spin (IS) ($t_{2g}^5 e_g^1$, S=1) or High Spin (HS) ($t_{2g}^4 e_g^2$, S=2) state[1]. The magnetic susceptibility of $LaCoO_3$ increases gradually showing a maximum at about 90 K indicative of the first spin state transition and follows a Curie-Weiss law thereafter. The second spin state transition occurs at around 500K where the material turns metallic with an increased effective moment [2]. The nature of these spin state transitions are controversial and debates exists over the first excited state being either an orbitally ordered IS state [3, 4] or a triply degenerate HS state [5].

The magnetic susceptibilities of $LaAl_{1-x}Co_xO_3$ have been investigated by Kyomen et.al to find that the LS states of Co^{3+} were stabilized by Al substitution [6]. Here were present the structural and low temperature transport studies of $LaAl_{1-x}Co_xO_3$ with regards to the spin states of Co^{3+} to understand the nature of charge transport in this compound.

EXPERIMENT

Polycrystalline $LaAl_{1-x}Co_xO_3$ (x = 0.2, 0.5, 0.8, 1) samples were synthesized by conventional solid state reaction starting with high purity precursors (4N). Stoichiometric quantities of La_2O_3, Al_2O_3 and Co_3O_4 were weighed, dry mixed, calcined and sintered with intermittent grinding at each temperature. The final sintering was performed on the cold pressed green pellets at 1300 °C in air. These pellets were crushed to powder on which the Powder X-ray diffraction data was collected using Rigaku MiniFlex-II tabletop diffractometer with CuKα radiation. The P-XRD data was refined using FullProf software. The low temperature dc transport measurements were done on the pellets by four probe method using a closed cycle refrigerator of APD cryogenics from room temperature down to 100 K.

RESULTS AND DISCUSSION

Structural Characterization

The unit cell dimensions obtained from the refinement have been presented in the Table 1 for all the samples. Figure 1 shows the Rietveld refined pattern for $LaAl_{0.5}Co_{0.5}O_3$. To maintain the brevity of the paper other refined patterns are not presented here. From the Rietveld analysis it is found that the samples with x = 0.2, 1 of the series are single phase with rhombohedral symmetry (R-$3c$). However, the samples

Solid State Physics
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TABLE 1A. Rietveld refined unit cell dimensions and the Co-O bond lengths for the rhombohedral structure of $LaAl_{1-x}Co_xO_3$.

Sample	a (Å)	b (Å)	c (Å)	Volume (Å^3)	Co-O bond length (Å)	χ^2
$LaAl_{0.8}Co_{0.2}O_3$	5.3652	5.3652	13.1158	326.9590	1.8948(8)	4.11
$LaAl_{0.5}Co_{0.5}O_3$	5.3666	5.3666	13.1338	327.5761	1.89734(15)	5.48
$LaAl_{0.2}Co_{0.8}O_3$	5.3579	5.3579	13.3363	331.5478	1.90506	9.52
$LaCoO_3$	5.4389	5.4389	13.0823	335.1527	1.92562	3.72

TABLE 1B. Rietveld Refined unit cell dimensions and the Co-O bond lengths for the monoclinic structure of $LaAl_{1-x}Co_xO_3$.

Sample	a (Å)	b (Å)	c (Å)	β	Volume (Å^3)	Co-$O_{(1)}$(Å)	Co-$O_{(2)}$(Å)	Co-$O_{(2)}$(Å)	χ^2
$LaAl_{0.5}Co_{0.5}O_3$	5.3806	5.4320	7.6389	90.847	223.2430	1.9288(7)	1.9873(7)	1.8750(6)	5.48
$LaAl_{0.2}Co_{0.8}O_3$	5.3679	5.4271	7.6354	90.911	222.4070	1.92783	1.98427	1.87167	9.52

with x = 0.5 and 0.8 exhibits mixture of rhombohedral and monoclinic phase ($I2/a$) of $LaAl_{1-x}Co_xO_3$ with 68.81% and 68.94% fractional percentage of rhombohedral phase respectively. The formation of rhombohedral and monoclinic mixed phase is indicative of the fact that it is not possible to create single phase samples of $LaAl_{1-x}Co_xO_3$ having higher Co concentration (Co ≥ 50%) using conventional solid state reaction synthesis because of the high distortion inherently induced in the system by the addition of Al and not a coherent Jahn- Teller distortion as reported earlier in $LaCoO_3$ [4]

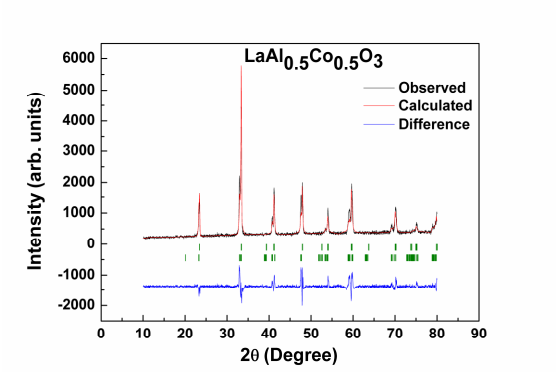

FIGURE 1. The Rietveld refined profiles for $LaAl_{0.5}Co_{0.5}O_3$. The black line in the profile indicates the experimental data, the red line indicates the fitted data using FullProf software and the blue line indicates the difference between the experimental and fitted value. The olive green line indicates the Bragg peaks.

There is a gradual increase in the unit cell volume and Co-O bond lengths with increase in the Co concentration for the rhombohedral structure of $LaAl_{1-x}Co_xO_3$ owing the bigger ionic radii of the cobalt in comparison to aluminium. Also the doped samples showed an increase in the c axis parameter compared to pure $LaCoO_3$ owing to the distortion induced by doping. With regard to the monoclinic phase no specific correlation was observed for the refined data.

DC Transport Measurements

The DC resistivity–temperature profile of $LaAl_{1-x}Co_xO_3$ for x = 0.5, 0.8, 1 is shown in Fig. 2. The sample with x = 0.2 was highly insulating. The profile shows that the resistivity of the samples increases with decrease in temperature in a semiconducting fashion. The resistivities are seen to increase gradually with a decrease in cobalt concentration indicating decrease in carrier concentration which is originally small polarons of holes created by excitation of electrons from the narrow π* bands formed by the Co^{3+} LS states to the Co^{3+} HS state which becomes Co^{2+} ($3d^7$) trapping the electron [2]. The resistivity data fits to the small polaron hopping model which follows the equation [7, 8],

$$\rho = \rho_\alpha T e^{\frac{E_p}{k_B T}} \qquad (1)$$

Where, ρ is the resistivity of the sample, $\rho_\alpha = \left(\frac{k_B}{\upsilon_{ph} N^2 e^2 R^2 C(1-C)}\right) e^{2\alpha R}$, k_B is the Boltzmann constant, E_p is the activation energy and T is the absolute temperature. N is the number of ion sites per unit volume, R is the average intersite spacing obtained from the relation R= $(1/N)^{1/3}$, C is the fraction of sites occupied by a polaron, α is the electron wave function decay constant obtained from fitting the experimental conductivity data, and υ_{ph} is the optical phonon frequency . A plot of ln (ρ/T) vs 1/T is apparently a straight line, the slope of which gives the activation energy E_p and the Debye temperature which is calculated from the point in the Arrhenius plot where the deviation from the linear behavior begins as shown in the Figure 3. The reduction in carrier concentration is evident from the increased activation

energy required for hopping as seen from Table 2. The Debye temperatures are also tabulated along with activation energies. Another reason or the decrease of charge carriers can be the presence of aluminium which is said to stabilize the LS states of Co^{3+} thus reducing the occupancy of e_g orbitals [8]. The non-Arrhenius regime at low temperatures is a general manifestation of small polaron hopping where the conduction occurs by tunneling [9].

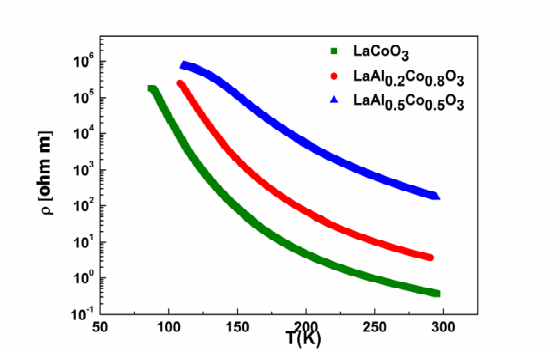

FIGURE 2. Low temperature resistivity profile of $LaAl_{1-x}Co_xO_3$.

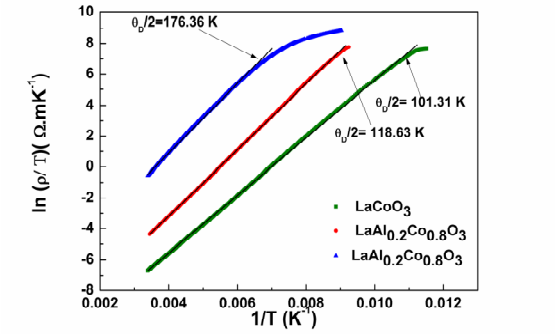

FIGURE 3. Arrhenius plot for Small polaron hopping model for $LaAl_{1-x}Co_xO_3$.The black dark line gives the Linear fit. The deviation from linear behavior starts at temperature $\theta_D/2$ as shown in figure.

CONCLUSIONS

The polycrystalline samples of $LaAl_{1-x}Co_xO_3$ were prepared by solid state reaction synthesis. The Rietveld refinement of the samples shows that $LaAl_{1-x}Co_xO_3$ with x = 0.2 & 1 were single phase with rhombohedral space group *R -3 c* and for x = 0.5 & 0.8 the samples were highly distorted with a combination of rhombohedral and monoclinic structure (*I2/a*). The electrical transport has been studied and it has been concluded that for samples with x = 0.5, 0.8, 1 the conduction is by small polaron hopping mechanism.

TABLE 2. Activation Energies and Debye temperature calculated from the Arrhenius plot

Sample	Activation energy (eV)	Debye Temperature (θ_D) (K)
$LaAl_{0.5}Co_{0.5}O_3$	0.1980	352.72
$LaAl_{0.2}Co_{0.8}O_3$	0.1848	237.26
$LaCoO_3$	0.1616	202.42

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