Crystal structure and electrical transport properties of single layered perovskite LaSrCoO$_4$

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Abstract. We present here investigations on the influence of structure on electrical transport properties of polycrystalline LaSrCoO$_4$ that is single layered perovskite with K$_2$NiF$_4$ type structure synthesized using solid state reaction route. Using Reitveld refinement of X-ray diffraction (XRD) data, it is found that the sample is in single phase with tetragonal structure (space group $I4/mmm$). Electrical resistivity performed in the temperature range 140 -300K shows semiconducting character of the sample. Considerable contrasts in the Co-O bond length is associated with the intermediate spin (IS) state of Co ion that correlates the structural and transport properties. Detailed analysis indicates that the temperature dependent electrical resistivity follows the three-dimensional variable range hopping (VRH) model in low temperature region below 225K. The high temperature (225 -300K) resistivity data has been found to follow the thermally activated behaviour.

1. Introduction

Compounds which crystallize in the tetragonal K$_2$NiF$_4$ type structure are the members of Ruddlesden-Popper series (ABO)$_n$(AO)$_n$ with $n=1$ known as single layered perovskites. Since the discovery of high temperature superconductivity in cuprate [1], these types of structures have been the subject of intense research. In single layered perovskite La$_2$CoO$_4$ structure, CoO$_6$ octahedron are connected by corner-sharing oxygen atoms to form a two dimensional CoO$_2$ layers which are separated by the rock salt structure type LaO slabs.[2].

An extra degree of freedom that comes on top of the orbital, spin (up or down) and charge degree of freedoms (that makes manganese and cuprate systems so exciting), is the spin state degree of freedom that distinguish the cobaltate from the other similar systems. Cobalt ion can exist in the three spin states, i.e. low spin (LS), intermediate spin (IS) and high spin (HS) depending on the competition between crystal field splitting and the on-site Coulomb exchange or Hund’s coupling [2]. Considerable research efforts have been made on cobalt containing layered structures La$_{2-x}$Sr$_x$CoO$_4$ because of interesting properties similar to manganese and copper containing layered oxides like colossal magnetoresistance [3] and superconductivity [4]. The single layered perovskite La$_{2-x}$Sr$_x$CoO$_4$ contains mixed valent state of cobalt ion i.e. Co$^{3+}$ and Co$^{5+}$ in (1-x):x ratio. For Co$^{5+}$ in LaSrCoO$_4$ compound (x=1) there is controversy in literature regarding spin state, it has been proposed to be in either intermediate spin state [5] or in a mixture of low spin and high spin states [6].

Consider the information about spin states of LaSrCoO$_4$ compound we have planned to understand the structure and electrical transport behaviour of this single layered perovskite. We
present here the detailed analysis and study of LaSrCoO$_4$ by means of room temperature X-ray diffraction and temperature dependent resistivity measurement in the range 140-300K. A possible correlation between structure and transport based on the already known spin state of the Co ions is proposed.

2. Experimental details
Polycrystalline sample LaSrCoO$_4$ has been synthesized by employing solid state route. Stoichiometric mixture of high purity La$_2$O$_3$, SrCO$_3$ and Co$_3$O$_4$ was grinded and calcined for 8 hours at 1000°C. After calcination the obtained powder was re-grinded, palletized in 10 mm disc and sintered for 12 hours at 1150°C.

The room temperature X-ray diffraction have been done using Bruker D2 Phaser in 2θ range 20°-80°, step size 0.02° with Cu Kα radiation (λ=1.54 Å). The diffraction pattern was analysed by Reitveld technique [7] using FULLPROF code. Temperature dependent resistivity was done using standard four probe method in the temperature range 140-300K.

3. Results and Discussion
Figure 1 shows the Reitveld refined XRD pattern of LaSrCoO$_4$, which reveals that the sample is in single phase having space group $I4/mmm$ (space group no. 139). From figure 1, it is clear that the calculated pattern is in excellent agreement with the experimentally observed pattern. The estimated lattice parameters $a$ and $c$ from the refinement are 3.8055 Å and 12.5010 Å, respectively. In the crystal structure of LaSrCoO$_4$ the Co ions are surrounded by oxygen in the octahedral symmetry with four O1 oxygen in the equatorial plane and two O2 oxygen in the apical direction along the $c$-axis of the unit cell resulting two different Co-O bond lengths one along the $c$-axis Co-O2 and other in the $ab$ plane Co-O1. From the refinement results we have found Co-O2 and Co-O1 are 2.0085 Å and 1.9027 Å, respectively. The ratio of these bond lengths i.e. Co-O2/Co-O1 is ~1.055 indicating the elongation of CoO$_6$ octahedron. We may correlate this distortion with the occupation of $e_g$ orbital [8]. Elongation of octahedron along the $c$-axis indicate about the IS of Co$^{3+}$ ion containing non-equivalent electrons in $e_g$ orbital, yielding Jahn-Teller distortion [8].

Electrical resistivity of sample in the range 140-300K is shown in figure 2, which shows the semiconducting nature of the sample. Inset (Figure 2) shows the derivative of resistivity curve. Anomaly at around 225K indicates a possibility of change in conductivity mechanism. For further detail analysis, resistivity data has been plotted in such way so that typical conductivity behaviour can be inferred. From the plot of ln$\rho$ against 1/T in Figure 3, the curve deviates from linearity. It is clear

**Figure 1.** Room temperature Reitveld refined XRD pattern of LaSrCoO$_4$. 

![Figure 1. Room temperature Reitveld refined XRD pattern of LaSrCoO$_4$.](image-url)
Figure 2. Temperature dependent electrical resistivity

that the high temperature (above 225K) resistivity data can be well fitted by the thermally activated conduction law, which follow the following form, equation (1).

$$\rho(T) = \rho_o \exp\left(\frac{E_a}{k_B T}\right)$$  \hspace{1cm} (1)

Where $E_a$ represent the activation energy and $k_B$ is the Boltzmann constant. The estimated value of activation energy $E_a$ is 211meV.

Figure 4 shows the plot of $\ln\rho$ vs $T^{-1/4}$ reveals that the low temperature (below 225K) resistivity follow the Mott’s three dimensional variable range hopping model which have following form, equation (2).

$$\rho(T) = \rho_o \exp\left(\frac{U}{T^{1/4}}\right)$$  \hspace{1cm} (2)

Where $U$ represent the fitting parameter.

The high value of electrical resistivity is the signature of absence of mobile charge carriers. For tetragonally elongated CoO$_6$ octahedron, we may expect that there is less repulsion between Co ion and oxygen ligand along the $z$ coordinate so to attain stability $d_{xz}, d_{yz}$ and $d_{3z^2-r^2}$ may shifted to lower energy. Simply we can say that degeneracy of $e_g$ orbital is lost and it has been reported previously that, if electrons in orbitals other than $3d_{x^2-y^2}$ tend to be localized, one may expect the semiconducting behaviour [9].
4. Conclusion
We have successfully synthesized polycrystalline LaSrCoO$_4$ sample using solid state reaction route. Reitveld refinement confirms that the sample is in single phase with tetragonal K$_2$NiF$_4$ type structure. The lattice parameters and bond lengths have been obtained from refinement. The difference between two Co-O bond lengths shows the distortion of CoO$_6$ octahedron, which gives an idea about the presence of IS state of Co$^{3+}$ ion in our sample. Temperature dependent resistivity shows the semiconducting behaviour of the sample. Detailed analysis revealed that it follow the three dimensional Mott’s variable range hopping formula below 225K and thermally activated conduction law with activation energy 211meV in high temperature region (above 225K).

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5. References
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