

# Rare Earth Sm<sup>3+</sup> Doped LaCoO<sub>3</sub> Cobaltite: Synthesis and Characterizations

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**Abstract:** Perovskite Cobaltite La<sub>0.95</sub>Sm<sub>0.05</sub>CoO<sub>3</sub>(LSCO) has been reported. The solid state reaction route has been employed and the sample formation has been confirmed via x-ray diffraction characterization. The XRD data investigation revealed the mono-phase rhombohedral structure (*R-3c*). The distorted rhombohedral structure for La<sub>0.95</sub>Sm<sub>0.05</sub>CoO<sub>3</sub> was further verified via Raman spectroscopic measurement. The dielectric measurement conveys good dielectric nature. The *ac* conductivity measurement reveals constant value of *acat* lower value of frequency but after a certain value of frequency, there is abrupt increase in the conductivity due to charge liberation at higher values of applied field. The four-probe *dc* measurement reveals the sample to be semiconducting in nature.

**Keywords:** Cobaltites, Structure, X-ray Diffraction, Four-probe Resistivity,

## INTRODUCTION

Cobalt oxides with a perovskite structure are endowed with interesting catalytic, ion conduction, magnetic, and semiconducting properties. Perovskites of the type LnREO<sub>3</sub> where Ln is rare earth element and a RE is rare earth metal have attracted the attention of the researchers in the recent past due to their potential applications in solid oxide fuel cells where they are used as electrodes, sensors etc. Perovskite based on the LaCoO<sub>3</sub> cobaltites exhibits intriguing electrical and electro-catalytic properties in addition to which they also exhibit high electrical conductivity and worth ionic conductivity expected to exceed the conductivity of the electrolyte materials in use. To achieve the better performance and the useful functional properties, it is necessary that the synthesized materials be dense with well controlled stoichiometry [1-4].

As the presence of secondary phases in the sample reduces the multi-functional character, we prefer single-phase materials. Due to their exceptional character, the Lanthanum cobaltite materials are the new interest of the materials scientists. Attempts have been made by the researchers to meet the requirements via modification in the synthesis process, temperature effects, particle size dependence etc. The most conventional sample synthesis procedure is high temperature solid-state reaction (SSR) route with thermal treatments upto 1200 °C and intermediate grindings [5,6]. In the present work, SSR route was used to prepare the Sm doped LaCoO<sub>3</sub> and its structural, vibrational, dielectric nature and temperature dependent transport property is discussed.

## EXPERIMENTAL DETAILS

The polycrystalline La<sub>0.95</sub>Sm<sub>0.05</sub>CoO<sub>3</sub> cobaltite was prepared via solid state reaction route. The starting materials were Sm<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub> of analytic grade and high purity and were used without pre-heating. The stoichiometric amounts were weighed and mixed in an agate-mortar with a grinding duration of 6h. The sample was calcined at 1000 °C for 10h. The sample was further ground for 6h and fired to a temperature of 1200 °C for 10h. Furthermore, the mixture was subjected to final grinding for an hour and was pelletized under the hydraulic press at a pressure of 7Tonnes/inch. The pellet were 10mm in diameter and nearly of 1mm thickness. The Pellet was then

sintered at 1300°C and silver pasted for dielectric measurements. Also the pellet was cut in rectangular bar of the length 6mm and cross section area of 1.2 mm<sup>2</sup>.

To confirm the phase formation, crystal structure and crystallite size of the compound La<sub>0.95</sub>Sm<sub>0.05</sub>CoO<sub>3</sub>, X-ray powder diffraction technique at room temperature using a Bruker D8-Advance X-ray diffractometer with CuK $\alpha$ 1 (1.5406 Å) radiation has been employed. The data was obtained with a step size of 0.02 over the angular range 2 $\theta$  (20° < 2 $\theta$  < 80°) generating X-ray by 40 kV and 40 mA power settings. For further confirmation of the structure, Raman characterization was carried out using the micro Raman system, Jobin Yvon Horiba LABRAM-HR visible (400–1100 nm), with argon (488 nm) as the excitation source. The dielectric properties were measured at room temperature in the frequency range 20Hz-10MHz using Wayne Kerr, Model 6500B, Precision Impedance Analyzer. Fourier Transformation Infrared Spectroscopy (FTIR) was done by Perkin Elmer FT-IR/FIR spectroscopy in the range of 400 to 4000 cm<sup>-1</sup>. The low temperature resistivity measurements were carried out using the laboratory made four probe setup.

## RESULTS AND DISCUSSIONS

The highly crystalline perovskite La<sub>0.95</sub>Sm<sub>0.05</sub>CoO<sub>3</sub> cobaltite was successfully synthesized via conventional high temperature solid state reaction route. The sample was X-ray diffraction characterized to confirm the type of phase and the structure of the sample so prepared. The analysis of the XRD spectrum displayed in Figure 1 revealed the single phase of the sample and the crystallization of the sample into the rhombohedral structure with the space group *R*-3c. The lattice parameter calculation revealed the values of a=b= 5.5526 Å and c=13.155 Å. Further the intense characteristic peak is the witness of the highly crystalline nature while the narrowness of the FWHM is the signature of the higher average crystallite size [7, 8]. The average crystallite size was calculated from the classical Scherer's formula,  $t = k\lambda/\Delta\cos\theta$ , where t is the crystallite size, k = 0.9 and is called the shape factor,  $\Delta$  is FWHM while as the  $\theta$  is Bragg angle. The calculated particle size was found to be 45nm.

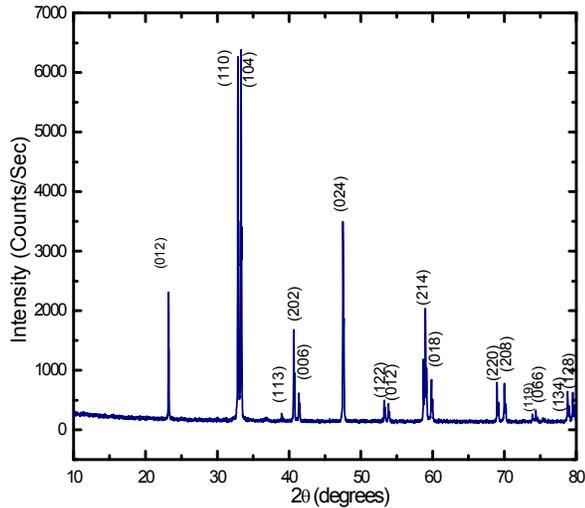


FIGURE 1 XRD pattern of LaSmCoO<sub>3</sub>

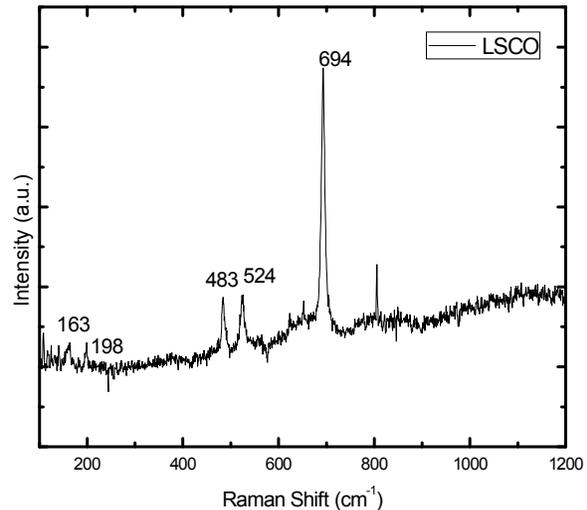


FIGURE 2. Raman Spectrum Of LSCO

To study the vibrational properties, the La<sub>0.95</sub>Sm<sub>0.05</sub>CoO<sub>3</sub> cobaltite was analyzed by micro-Raman spectroscopy. Raman spectrum of the synthesized cobaltite is shown in the Figure 3. The irreducible representation of the phonon modes of the rhombohedrally distorted perovskite structure of LaCoO<sub>3</sub> at the  $\Gamma$  point is given by [9]:

$$\Gamma = 2A_{1u} + 3A_{2g} + A_{1g} + 3A_{2u} + 4E_g + 5E_u$$

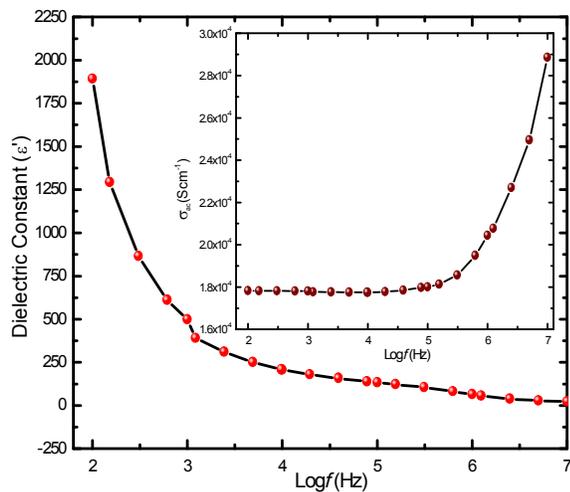
Among these vibrational modes, the  $A_{1g}$  and  $E_g$  are Raman active, and the  $A_{2u}$  and  $E_u$  are infrared active; the other modes are silent. The Raman signal at 163 cm<sup>-1</sup> is assigned to the  $A_{2g}$  stretching mode of La atoms, the broad band at 694 cm<sup>-1</sup> corresponds to the  $A_{2g}$  breathing mode.

For the rhombohedral  $\text{LaCoO}_3$ , only the  $A_{1g}$  and  $E_g$  modes are Raman active [9, 10]. Podobedov et al. assigned the peak at  $694\text{ cm}^{-1}$  to the second-order Raman scattering. The intensity of the Raman peak at  $694\text{ cm}^{-1}$  may be caused by the crystal perfection at high calcination temperature and the increased particle size.

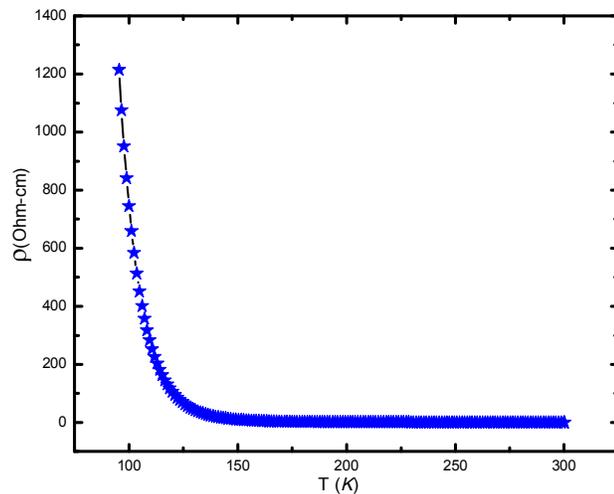
Two broad modes and a sharper mode, located at  $694$ ,  $524$ , and  $483\text{ cm}^{-1}$  were observed assigned to  $A_{2g}$  breathing,  $E_g$  quadrupole (JT) and  $E_g$  bending modes. For Raman scattering of the rhombohedral  $\text{La}_{0.95}\text{Sm}_{0.05}\text{CoO}_3$  perovskite, the two  $524$  and  $694\text{ cm}^{-1}$  bands can be assigned to local Jahn-Teller distortions in the semiconducting phase; the absence of these bands is an indication of the metallic state of the material. The disappearance of the two broad peaks reflects the transition to a dynamically less distorted local structure in the metallic phase [9-11].

The dielectric constant ( $\epsilon'$ ) is the measure of the amount of energy stored in a dielectric material due to the applied field. It is calculated by formula  $\epsilon = Ct/A\epsilon_0$  where  $\epsilon_0$  is the permittivity of free space, 't' is the thickness of pellet, 'A' is the cross sectional area and 'C' is the capacitance of pellet. Figure 2 shows the variation of dielectric constant ( $\epsilon'$ ) with frequency for  $\text{La}_{0.95}\text{Sm}_{0.05}\text{CoO}_3$  at room temperature. Usual trend of decrease in dielectric constant ( $\epsilon'$ ) with increase in frequency (f) is observed from the plot and dielectric constant becomes independent of frequency at higher values of frequency. This variation of  $\epsilon'$  with logarithm of frequency reveals the dispersion due to Maxwell-Wagner type interfacial polarization and is in agreement with Koop's phenomenological theory [12].

The *ac* conductivity vs  $\log f(\text{Hz})$  is shown in Figure 3. The plot reveals initially low and constant value of the conductivity and after a certain value of frequency, the conductivity increases abruptly. This character can be attributed to the activation of hopping of charge carriers between different localized sites due to the increase in the applied field. With increase in applied field, the immigration of electrons enhances which increases the conductivity at higher frequency values [13].



**FIGURE 3.** Dielectric constant and ac conductivity (inset) of LSCO



**FIGURE 4.** Temperature dependent dc resistivity

The  $\text{La}_{0.95}\text{Sm}_{0.05}\text{CoO}_3$  perovskite was examined for the resistivity using conventional four probe technique. The measurement was carried out in the temperature range of  $100\text{ K} - 300\text{ K}$ . The data has been plotted and displayed in the Figure 4. The behaviour of the sample under the limits of experiment displays the semiconducting nature [13, 14]. The parent  $\text{LaCrO}_3$  is P-type semiconducting material, the current sample confirms the same. It is worthwhile to mention here that the effect of rare earth Sm doping has not changed the nature that may be due to the minimum doping level. The semiconducting character is hereby first verified via the Raman spectral analysis and then by the resistivity measurements.

In conclusion, polycrystalline single phase of  $\text{La}_{0.95}\text{Sm}_{0.05}\text{CoO}_3$  cobaltite was prepared and has been found to exhibit distorted rhombohedral structure with space group  $R-3c$ . The Raman scattering revealed the sample formation with semiconducting phase due to the presence of  $524\text{ cm}^{-1}$  and  $694\text{ cm}^{-1}$ . The dielectric measurement confirms the worth dielectric constant and high *ac* electrical conductivity which confirms its application in the power generation from waste energy using Seebeck concept. The semiconducting nature was further verified via *dc* resistivity measurement.

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