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# Sign change of the thermoelectric power in LaCoO<sub>3</sub>

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**Abstract.** The substitution of 1%-Ce<sup>4+</sup> for La<sup>3+</sup> in LaCoO<sub>3</sub> is found to change the sign of the Seebeck coefficient at room temperature. This demonstrates that not only holes but also electrons can be created in LaCoO<sub>3</sub>. The result is compatible with the Heikes formula for doping levels close to the “pure” trivalent Co<sup>3+</sup> state. Nonetheless, the physical properties such as magnetic susceptibility, magnetization, thermal conductivity and resistivity are found to be asymmetric for hole and electron-doped LaCoO<sub>3</sub>. Such a different behaviour is ascribed to the very different spin-states of Co<sup>4+</sup> (low-spin,  $t_{2g}^5 e_g^0$ ) and Co<sup>2+</sup> (high-spin,  $t_{2g}^5 e_g^2$ ).

The richness of the physical properties found in the cobaltites, exemplified by the recent discovery of superconductivity in Na<sub>0.3</sub>CoO<sub>2</sub>·1.3H<sub>2</sub>O [1] originates from the cobalt cations ability to adopt several oxidation- and spin-states. In particular, the LaCoO<sub>3</sub> perovskite provides a classical example for thermally assisted spin state transitions of the trivalent cobalt [2,3]. Its ground state is a nonmagnetic insulator with only low-spin (LS) Co<sup>3+</sup>, but its magnetic susceptibility increases with temperature up to 100 K as a result of a transition from LS to intermediate-spin (IS) state. A second spin-state transition is then inferred from a change in the transport properties at about 500 K from an activated regime ( $\sim 0.1$  eV at 100 K) to a metallic regime ( $\sim 1$  m $\Omega$  cm) beyond 500 K corresponding to a conversion to high-spin (HS) [4,5]. The energy closeness of the different Co<sup>3+</sup> spin-states (LS, IS, HS), illustrated by these two spin-state transitions, is also revealed by the drastic effect of a low amount of doping upon the physical properties [4]. For instance, via the substitution of only 1% of Sr<sup>2+</sup> for La<sup>3+</sup> in La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3</sub>, i.e. as the cobalt oxidation state goes from 3.00 to 3.01, the transition to the non-magnetic LS ground state below 100 K is suppressed. Instead the increase of the magnetic susceptibility, linked to the presence of spin-polarons created around the Co<sup>4+</sup> defects, is observed.

The thermoelectric power (TEP) measurement is a good technique to probe the charge carriers in the low doping region for which the conduction is made by small polaron. In this case [6], the high temperature-independent TEP (Seebeck,  $S$ ) can be described by the Heikes formula,  $S = -(\frac{k_B}{e}) \ln[\frac{1-x}{x}]$ , where  $x$  is the fraction of cobalt site occupied by a charge carrier. Thus, the  $S$  sign and value

give a direct information about the nature (holes vs. electron) and concentration of the charge carrier. It must be also pointed out that both types of carriers may be present but with only one dominating. According to the Heikes expression, it is obvious that only small changes of carriers content may make the TEP changing. Additionally, as shown by the Sr<sup>2+</sup> for La<sup>3+</sup> substitution in La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3</sub> [4], these subtle changes of charge carrier content may also affect the “apparent” trivalent cobalt spin state, since for Co<sup>3+</sup> species a transition from LS towards a higher spin-state for the six neighbors of a Co<sup>4+</sup> is induced.

According to the work by Senaris-Rodriguez and Goodenough [3], the TEP in LaCoO<sub>3</sub> is positive and large, i.e. holes are dominating. In order to try to reverse the TEP sign, in the present communication, minute substitutions of tetravalent cations (Ce<sup>4+</sup>, Th<sup>4+</sup>) for La<sup>3+</sup> in LaCoO<sub>3</sub> are reported. It is found that negative and large absolute  $S$  values can be obtained in LaCoO<sub>3</sub>. These results are also compared to the Sr<sup>2+</sup> for La<sup>3+</sup> substitution. In contrast to the holes creation that promotes a ferromagnetic behavior, for the electron doped LaCoO<sub>3</sub> phase, the Co<sup>3+</sup> spin-state transition to the LS state is preserved. These results are discussed in the light of the recently proposed spin blockade mechanism for the oxygen deficient perovskite, containing trivalent cobalt, HoBaCo<sub>2</sub>O<sub>5.5</sub>, which exhibits a TEP sign change at the metal-insulator transition [7].

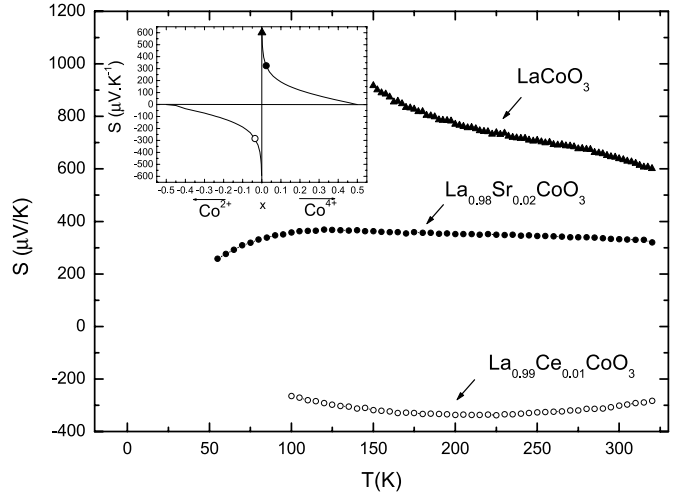
Polycrystalline samples of LaCoO<sub>3</sub>, La<sub>0.99</sub>Ce<sub>0.01</sub>CoO<sub>3</sub> and La<sub>0.98</sub>Sr<sub>0.02</sub>CoO<sub>3</sub> were prepared via solid state reaction. The precursor La<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub> and SrO<sub>2</sub> or CeO<sub>2</sub> were mixed in the stoichiometric ratio. They were heated at 1000 °C for 4 h and at 1100 °C for 10 h. Then the

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products were pressed in the form of bars under 1 ton/cm<sup>2</sup> and heated again at 1250 °C for 20 h. The structures were characterized at room temperature (RT) by using a Philips X-ray diffractometer using CuK $\alpha$ . The lattice parameters were obtained from the Rietveld analysis of the X-ray data. Electron diffraction (ED) and energy dispersive spectroscopy (EDS) investigations were carried out at RT with a JEOL 200 CX electron microscope equipped with KEVEX analyzer. The thermal conductivity ( $\kappa$ ) and Seebeck coefficient were measured simultaneously by using a steady-state method. The values of  $\kappa$  are raw data (not corrected from porosity effect). Resistivity data were collected with the four-probe technique. Quantum Design magnetometers were used to collect the ac magnetic susceptibility and dc magnetization data.

The cation composition of the sample has been investigated by EDS for about twenty crystallites. The resolution of the KEVEX analyzer limits the accuracy of the cation analysis. Therefore one must be very cautious about the contents of cerium and strontium. Although the EDS results show that Ce or Sr are substituted in the lattice, some CeO<sub>2</sub> impurities are detected in the case of La<sub>0.99</sub>Ce<sub>0.01</sub>CoO<sub>3</sub>. The La/Co ratio tends to be close to the nominal composition in the EDS accuracy. The R $\bar{3}c$  space group is confirmed by the ED study. Structure refinements of the samples from X-ray data were performed with the R $\bar{3}c$  space group. Some extra peaks corresponding to the cerium oxide are also detected. The lattice parameters remain very similar to those of LaCoO<sub>3</sub>, for instance, the lattice parameters for LaCoO<sub>3</sub> and La<sub>0.99</sub>Ce<sub>0.01</sub>CoO<sub>3</sub> are ( $a = 5.4428 \text{ \AA} / c = 13.0506 \text{ \AA}$ ) and ( $a = 5.4426 \text{ \AA} / c = 13.0884 \text{ \AA}$ ), respectively.

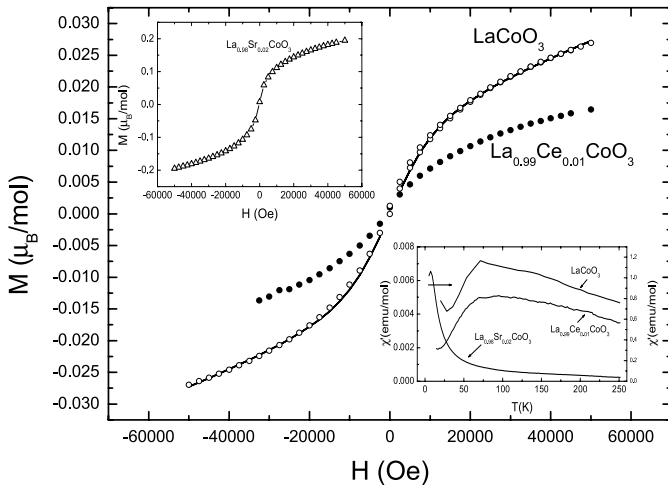
The TEP of LaCoO<sub>3</sub>, La<sub>0.99</sub>Ce<sub>0.01</sub>CoO<sub>3</sub> and La<sub>0.98</sub>Sr<sub>0.02</sub>CoO<sub>3</sub> as a function of temperature are given in Figure 1. With our experimental set-up, the TEP can be measured only when the resistivity of the samples is smaller than 10<sup>4</sup>  $\Omega$  cm, which corresponds to  $T > 50 \text{ K}$ , 100 K or 150 K depending on the samples (see inset of Fig. 3). For all three compounds, the  $S(T)$  curves are found to be nearly temperature independent in the  $T$  range of the measurements (5 K–320 K). The major difference between these curves is the sign change of  $S$ , from  $S > 0$  for LaCoO<sub>3</sub> ( $S_{300 \text{ K}} = 640 \mu\text{VK}^{-1}$ ) and La<sub>0.98</sub>Sr<sub>0.02</sub>CoO<sub>3</sub> ( $S_{300 \text{ K}} = 332 \mu\text{VK}^{-1}$ ) to  $S < 0$  ( $S_{300 \text{ K}} = -302 \mu\text{VK}^{-1}$ ) in La<sub>0.99</sub>Ce<sub>0.01</sub>CoO<sub>3</sub>. This sign change suggests strongly that the nature of the charge carriers is hole-like and electron-like for the formers and the latter, respectively. Looking at the theoretical curves of the aforementioned Heikes formula represented in the inset of Figure 1, it becomes obvious that on both parts of the “pure Co<sup>3+</sup>” ideal stoichiometry, the largest absolute TEP values are realized when the hole or electron concentrations are the smallest. Even if the Heikes formula is valid at very high temperature, the value at 300 K,  $S_{300 \text{ K}}$ , can give a crude estimate of the carrier concentration. From the  $S_{300 \text{ K}}$  values, this formula yields fractions of  $9 \times 10^{-4}$  Co<sup>4+</sup> per cobalt in LaCoO<sub>3</sub>, attesting of the good stoichiometry of the pristine compound,



**Fig. 1.** Temperature dependence of the thermopower (Seebeck:  $S$ ), of LaCoO<sub>3</sub> (closed triangles), La<sub>0.99</sub>Ce<sub>0.01</sub>CoO<sub>3</sub> (open circles), La<sub>0.98</sub>Sr<sub>0.02</sub>CoO<sub>3</sub> (closed circles). Inset: Theoretical  $S(x)$  curves from the Heikes formula (see text),  $x$  is the fraction of electron (hole) per cobalt. The experimental points for LaCoO<sub>3</sub>, La<sub>0.99</sub>Ce<sub>0.01</sub>CoO<sub>3</sub> and La<sub>0.98</sub>Sr<sub>0.02</sub>CoO<sub>3</sub> are shown with the same symbols as the  $S(T)$  curves.

against  $2.2 \times 10^{-2}$  Co<sup>4+</sup>/Co and  $3.6 \times 10^{-2}$  Co<sup>2+</sup>/Co for La<sub>0.98</sub>Sr<sub>0.02</sub>CoO<sub>3</sub> and La<sub>0.99</sub>Ce<sub>0.01</sub>CoO<sub>3</sub>, respectively. The corresponding  $S$  values are reported in Figure 1. It should be mentioned that if in the case of the Sr doped LaCoO<sub>3</sub> compound, this value,  $2.2 \times 10^{-2}$  Co<sup>4+</sup>/Co, is close to the expected one,  $2.0 \times 10^{-2}$ , the larger difference in Ce doped sample reflects probably some uncertainty about the solubility of Ce in the structure. Nonetheless, these results demonstrate that with only low doping levels of divalent or tetravalent cations substituted for La<sup>3+</sup>, a clear TEP sign change is induced, reflecting the possibility to create holes or electrons in the Co<sup>3+</sup> based LaCoO<sub>3</sub> cobaltite. This result attributed to the tetravalent state of cerium which is responsible for the Co<sup>2+</sup> creation, is confirmed by the Th<sup>4+</sup> for La<sup>3+</sup> substitution that leads also to  $S < 0$  values ( $S = -118 \mu\text{VK}^{-1}$  at 300 K for La<sub>0.96</sub>Th<sub>0.04</sub>CoO<sub>3</sub>).

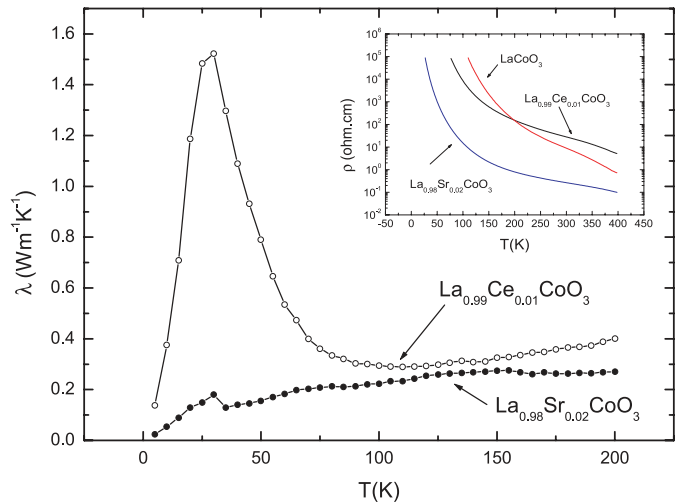
The different nature of the charge carriers has a direct consequence on the magnetic properties and, more precisely, on the spin-state transition observed below 100 K in LaCoO<sub>3</sub>. As shown in the right inset in Figure 2, the shape of the  $T$  dependent magnetic susceptibility ( $\chi$ ) curves is similar in the case of LaCoO<sub>3</sub> and La<sub>0.99</sub>Ce<sub>0.01</sub>CoO<sub>3</sub> but very different for La<sub>0.98</sub>Sr<sub>0.02</sub>CoO<sub>3</sub>. For LaCoO<sub>3</sub>, the  $\chi$  drop below 100 K is due to Co<sup>3+</sup> spin-state transition, from IS ( $S = 1$ ) to LS ( $S = 0$ ) with  $T$ . The similarity of this  $\chi(T)$  curve with that of La<sub>0.99</sub>Ce<sub>0.01</sub>CoO<sub>3</sub> shows that the Co<sup>3+</sup> spin-state transition is preserved even in the presence of  $\sim 3$ –4% of Co<sup>2+</sup>/Co. In contrast, the large  $\chi$  increase at low temperature on the  $\chi(T)$  curve of La<sub>0.98</sub>Sr<sub>0.02</sub>CoO<sub>3</sub> is consistent with previous reports showing that the hole-doping in LaCoO<sub>3</sub> tends to stabilize higher spin-states than LS for the Co<sup>3+</sup> species.



**Fig. 2.** Magnetic field ( $H$ ) dependence of the magnetization ( $M$ ) at 5 K for  $\text{LaCoO}_3$  (open circles),  $\text{La}_{0.99}\text{Ce}_{0.01}\text{CoO}_3$  (closed circles). Left inset:  $M(H)$  curve of  $\text{La}_{0.98}\text{Sr}_{0.02}\text{CoO}_3$  (open triangles). For  $\text{LaCoO}_3$ , the solid line is a fitting by the Brillouin function with the parameters given in the text. Right inset:  $T$  dependent magnetic susceptibility [ $\chi(T)$ ] of  $\text{LaCoO}_3$ ,  $\text{La}_{0.99}\text{Ce}_{0.01}\text{CoO}_3$  and  $\text{La}_{0.98}\text{Sr}_{0.02}\text{CoO}_3$ .

This tendency for hole-doping to create higher spin states is confirmed by the  $M$ - $H$  curves (Fig. 2). By using a Brillouin function similar to that used in reference [4] for  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ , a fitting curve is obtained for  $\text{LaCoO}_3$  and shown as a solid line in Figure 2. A hole number of  $1.0 \times 10^{-3} \text{ Co}^{4+}/\text{Co}$  is found, with a  $S$  spin quantum number of 7.5, a value higher than the expected one ( $S = 0$ ,  $S = 1$  and  $S = 2$  for  $\text{Co}^{3+}$  LS, IS, HS). Such a large spin value is consistent with the creation of spin polaron. On the other hand, the  $\text{Co}^{4+}$  concentration value is very close to that extracted from the Heikes formula. This confirms that the  $\text{LaCoO}_3$  cobaltite, in the present condition of preparation, exhibits a tendency towards “hole self-doping”. The creation of additional holes by the  $\text{Sr}^{2+}$  for  $\text{La}^{3+}$  substitution makes  $M$  increase remarkably as shown in the left inset of Figure 2 for  $\text{La}_{0.98}\text{Sr}_{0.02}\text{CoO}_3$  with  $M$  values an order of magnitude larger than those of  $\text{LaCoO}_3$ .

The very different effects induced by hole and electron are also illustrated by the  $T$  dependence of the thermal conductivity ( $\lambda$ ) curves (Fig. 3). A large  $\lambda$  increase is observed below 100 K in the Ce doped  $\text{LaCoO}_3$ , going through a maximum value at 25 K, whereas a much smoother  $\lambda(T)$  curve, with  $\lambda$  that decreases with  $T$ , is observed for  $\text{La}_{0.98}\text{Sr}_{0.02}\text{CoO}_3$ . In fact, in these cobaltites, the thermal conductivity is driven by the phonons and their scattering process. The low thermal conductivity values ( $\sim 1 \text{ WK}^{-1} \text{ m}^{-1}$  at 300 K) are comparable to those of glassy materials and are usually referred to phonon glass [9]. The  $\lambda$  increase below the spin-state transition is understood by considering the release of the coherent Jahn-Teller (JT) distortion as the  $\text{Co}^{3+}$  spin-state evolves from magnetic IS to non magnetic LS which favors the phonon propagation. The lower thermal conductivity at low  $T$  in  $\text{La}_{0.98}\text{Sr}_{0.02}\text{CoO}_3$  can be associated to the pres-

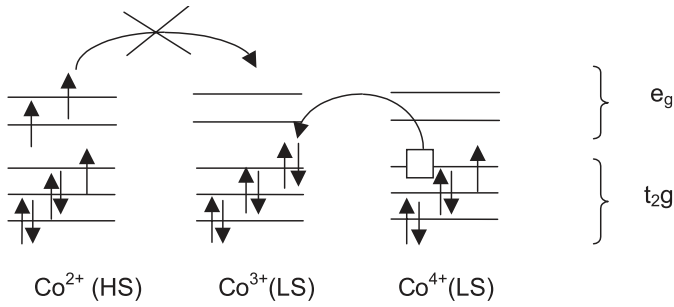


**Fig. 3.**  $T$  dependence of the thermal conductivity ( $\lambda$ ),  $\text{La}_{0.99}\text{Ce}_{0.01}\text{CoO}_3$  (open circles) and  $\text{La}_{0.98}\text{Sr}_{0.02}\text{CoO}_3$  (closed circles). Inset:  $T$  dependent resistivity ( $\rho$ ) curves.

ence of the spin polarons created by the low amounts of  $\text{Co}^{4+}$  whereas the  $\lambda$  increase below 100 K in Ce doped and pure  $\text{LaCoO}_3$  compounds can be understood as a disappearance of the JT distortion for the IS  $\text{Co}^{3+}$  which reduces the tilting and vibrations of the  $\text{CoO}_6$  octahedra affecting the phonon modes.

Finally, the comparison of the resistivity curves (inset of Fig. 3) shows that the doping by  $\sim 2\%$  holes in  $\text{LaCoO}_3$  affects more importantly the resistivity ( $\rho$ ) than the  $\sim 4\%$  electrons in  $\text{LaCoO}_3$ . At 300 K, the  $\rho$  value of  $\text{La}_{0.99}\text{Ce}_{0.01}\text{CoO}_3$ ,  $\rho_{300 \text{ K}} = 30 \text{ } \Omega \text{ cm}$ , is almost greater by a factor of  $10^2$  than that of  $\text{La}_{0.98}\text{Sr}_{0.02}\text{CoO}_3$ .

The present study demonstrates that a low concentration of charge carriers can be created in the stoichiometric  $\text{LaCoO}_3$  cobaltite by substituting either  $\text{Sr}^{2+}$  or  $\text{Ce}^{4+}$  for  $\text{La}^{3+}$ . From the TEP sign, it is found that these charge carriers are holes or electrons. Such a change from  $S > 0$  to  $S < 0$  was previously reported for  $\text{LaMnO}_3$ , in which, by only changing the annealing atmosphere,  $S$  was found to change from  $S = +550 \text{ } \mu\text{V K}^{-1}$  to  $S = -600 \text{ } \mu\text{V K}^{-1}$  [6]. Although electron and hole doped  $\text{LaCoO}_3$  exhibit symmetric TEP properties, in agreement with the Heikes formula, the magnetic behavior of these oxides is asymmetric. On one hand, the  $\text{Co}^{4+}$  holes tend to create a ground state with spin polarons of high spin values showing that the LS-state of the neighboring  $\text{Co}^{3+}$  is not retained [4]. On the other hand, the  $\text{Co}^{2+}$  ( $S = 3/2$ ) electrons, in the concentration of the present study, do not affect the  $\text{Co}^{3+}$  spin-state transition to LS as  $T$  decreases below 100 K. According to reference [8], the hole carrier,  $\text{Co}^{4+}$ , in the hybridized  $3d$ - $2p$  bands strongly couple with the  $3d$  spins. For the electrons type carriers, the contrasting effect on the magnetic properties show that the HS  $\text{Co}^{2+}$  do not couple so strongly with the surrounding  $\text{Co}^{3+}$ . This difference can be explained by a similar mechanism of spin blockade previously proposed for  $\text{LnBaCo}_2\text{O}_{5.5}$  [7]. In this pure trivalent cobaltite for reason of spin-states compatibility,



**Fig. 4.** Schematic spin-states configurations of  $\text{Co}^{3+}$  (low-spin),  $\text{Co}^{4+}$  (low spin) and  $\text{Co}^{2+}$  (high spin). From the figures, the hopping of one electron (HS  $\text{Co}^{2+}$ ) in the LS  $\text{Co}^{3+}$  matrix would involve several electrons and is thus forbidden.

it was shown that the hopping of LS  $\text{Co}^{4+}$  hole in a matrix of LS  $\text{Co}^{3+}$  is easier than that of a HS  $\text{Co}^{2+}$  electron (Fig. 4). Indeed, in the case of LS  $\text{Co}^{4+}$  in a matrix of LS  $\text{Co}^{3+}$ , a conduction band can be formed in the  $t_{2g}$  band as one can interchange a LS  $\text{Co}^{3+}$  and LS  $\text{Co}^{4+}$  by moving only one spin  $1/2$ . On the other hand, when  $\text{Co}^{2+}$  is created ( $\text{Co}^{2+}$  is always a HS ion), the hopping of only one electron in the  $e_g$  band is not possible without simultaneously flipping some other spins or change corresponding multiplets of the neighboring  $\text{Co}^{3+}$  states. One cannot interchange states with spins  $S = 0$  (LS  $\text{Co}^{3+}$ ) and  $S = 3/2$  (HS  $\text{Co}^{2+}$ ) by only moving one electron which carries spin  $1/2$ . Accordingly, the  $\text{Co}^{4+}$  coupling to the  $3d$  spins is greater than that of  $\text{Co}^{2+}$ . The retained IS to LS spin-state transition in the doped  $\text{LaCoO}_3$  is also corroborated by the thermal conductivity of the Ce substituted  $\text{LaCoO}_3$ , showing a  $\lambda$  increase as the Jahn-Teller IS- $\text{Co}^{3+}$  species gradually transform into less-distorted LS  $\text{Co}^{3+}$  octahedra as  $T$  decreases. On the opposite, for the hole-doped system,

since the JT distorted structure evidenced beyond 100 K in  $\text{LaCoO}_3$  is retained at lower  $T$ , according to the strong covalent character of  $\text{Co}^{4+}$ , the thermal conductivity values remain small below 100 K.

In conclusion, this study has shown that the substitution of  $\text{LaCoO}_3$  allows changing the sign of the thermoelectric power while keeping a large magnitude. This opens a new opportunity in the search for new n-type thermoelectric materials to be used for high temperature thermogenerator.

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