

# Magnetism, structure and transport of $Y_{1-x}Ca_xCoO_3$ and $La_{1-x}Ba_xCoO_3$ <sup>☆</sup>

J. Hejtmanek<sup>a,\*</sup>, Z. Jiráček<sup>a</sup>, K. Knížek<sup>a</sup>, M. Maryško<sup>a</sup>, M. Veverka<sup>a</sup>, H. Fujishiro<sup>b</sup>

<sup>a</sup>Institute of Physics of ASCR, Na Slovance 2, 182 21 Praha 8, Czech Republic

<sup>b</sup>Department of Materials Science and Technology, Faculty of Engineering, Iwate University, Morioka 020-8551, Japan

## Abstract

We compare the magnetic, structural and transport properties of  $La_{1-x}Ba_xCoO_3$  and  $Y_{1-x}Ca_xCoO_3$  perovskites. The experimental data supported by *ab initio* calculations reveal that: (i) Y-based perovskites are up to room temperature represented by essentially insulating LS state ( $T < 300$  K) followed by a gradual increase to IS state ( $S \sim 1$ ) with enhanced conductivity above 500 K, (ii) the magnetic interactions in La-based perovskites are antiferromagnetic with  $S \sim 1.5$  ( $T > 700$  K) and (iii) the Ba doping induces the ferromagnetic correlations and leads to a highly conducting state above 600 K.

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Since more than 40 years the spin-state of cobalt ions and the nature of two broad magnetic–electronic transitions in  $LaCoO_3$  have been investigated [1]. The low-temperature transition at  $T \approx 110$  K is unambiguously identified as the spin-state transition from low-spin ( $S = 0, t_{2g}^6$ ) to intermediate-spin ( $S = 1, t_{2g}^5 e_g^1$ )  $Co^{3+}$  configuration. On the other hand the origin of transition at  $T \approx 500$  K is not clearly established, although possible orbital ordering is proposed [2]. As both the average radius of interpolated large cation and the mean cobalt valency determine critically the magnetic, structural and transport properties, to identify the nature of spin and metal–insulator transitions in perovskite cobaltites we compare the high symmetry  $La_{1-x}Ba_xCoO_3$  ( $R\bar{3}c$  space group, Co–O–Co bond angle  $\sim 164^\circ$ ) and distorted  $Y_{1-x}Ca_xCoO_3$  ( $Pbnm$ ,  $\sim 148^\circ$ ). Moreover, the chemical

composition was chosen with respect to rule out the eventual role of RE-magnetism.

As the classical ceramic route, used for the synthesis of  $La_{1-x}Ba_xCoO_3$  ceramics, did not provide the single phase  $Y_{1-x}Ca_xCoO_3$  samples, these were prepared by the nitrate decomposition method. Magnetic and transport properties of the prepared La–Ba and Y–Ca perovskites were investigated over a broad temperature region up to 1000 K. The temperature dependence of magnetic susceptibility is in Fig. 1 compared with lines marking the characteristic spin states. The Ba doping converts the diamagnetic ground state of  $LaCoO_3$  to the paramagnetic one ( $S \approx 1.5$ ) which is accompanied by a low-temperature glass-like cusp at  $T_{SG} \approx 25$  K. Contrary to that, the Ca doping in Y–Ca system does not induce similar change of magnetic behavior and both samples preserve the low-spin ground state at low temperature. The LS–IS transition is gradual and shifted to higher temperature—from 400 to 800 K.

Electronic structure calculation [3] performed for various simulated structures of  $LnCoO_3$  showed, that the Co–O–Co bond angle is the most decisive for stabilization either LS or IS state. The critical value being  $\sim 163.5^\circ$  is in good agreement with experiment for

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\*Corresponding author. Institute of Physics of ASCR, Cukrovarnicka 10, CZ Praha 6, Praha 16253, Czech Republic. Tel.: +420-2-203-18-419; fax: +420-2-333-43-184.

E-mail address: [hejtman@fzu.cz](mailto:hejtman@fzu.cz) (J. Hejtmanek).

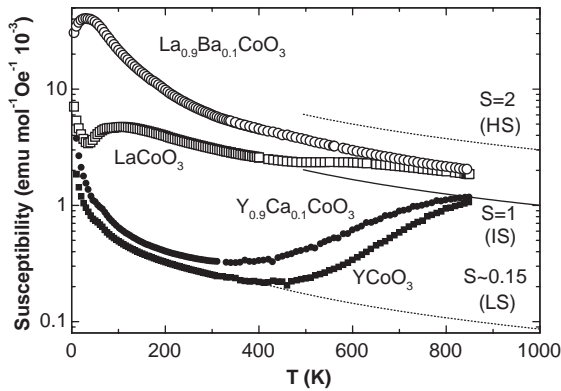


Fig. 1. The temperature dependence of the DC magnetic susceptibility (measured at 10 kOe) for  $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$  (open symbols) and  $\text{Y}_{1-x}\text{Ca}_x\text{CoO}_3$  (full symbols).

$\text{LaCoO}_3$ . However, for more distorted  $\text{YCoO}_3$  our calculation propose LS state for the whole temperature range and cannot explain the gradual LS–IS transition.

The Ca- and Ba-doping have a similar impact on the electrical resistivity compared with the parent perovskites, see upper panel of Fig. 2. The temperature dependence of electrical resistivity further demonstrates that the charge carrier transport is substantially hindered in distorted Y–Ca (Pbnm) system compared with La–Ba ( $R\bar{3}c$ ).

The character of the charge carrier conduction accompanying the phase transitions is evidenced by the thermopower data presented in lower panel of Fig. 2. Here, the metal–insulator transition (exemplified in the inset) is accompanied by a decrease of the thermopower from a large positive values, characterizing the activated hopping conduction at lower temperatures, to smaller values generally associated with degenerate charge carriers. The values of the thermopower undergoes also a distinct decrease upon Ba(Ca)doping when the decrease with decreasing temperature, in context with the temperature activated electrical resistivity, mirrors the variable range hopping of the charge carrier transport at low temperatures.

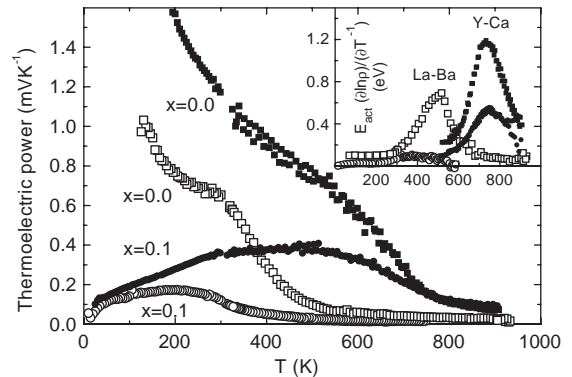
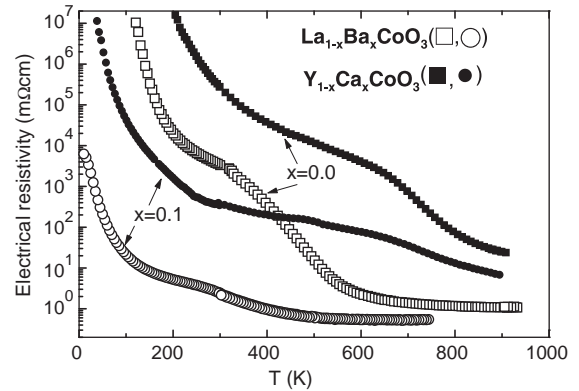


Fig. 2. The temperature dependence of the electrical resistivity (upper panel) and thermoelectric power (lower panel) for  $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$  (open symbols) and  $\text{Y}_{1-x}\text{Ca}_x\text{CoO}_3$  (full symbols). In the inset the M–I transition is evidenced via the activation energy of the electrical resistivity.

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