Dual nature of high-temperature electronic transport in layered perovskite-like cobaltites: exhaustive consideration of experimental features observed

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SUPPLEMENTARY INFORMATION

S1. General $Po_2 = f(\delta, T)$ relation for layered cobaltites

Defect chemistry of each oxide is known to be sufficiently dependent on its actual chemical composition. For instance, charge state of a particular impurity in a double cobaltite matrix can be expected to significantly influence on resulting expressions relating δ to external conditions. Therefore, model equations for every special case will be different. Nevertheless, some generalizations can be made assuming the specific charge states for added impurities are defined. For instance, it is reasonable to consider only 2+/3+ charged dopants for both A- and B-site positions because these cases have been studied most extensively in literature [1-3]. Accordingly, the chemical formula of double perovskite can be now written as $(LnBa)_{1-x}A_xCo_{2-y}B_yO_{6-\delta}$ with A and B standing for the dopants introduced into the respective sublattice. Then, generalized charge neutrality requirement can be formulated in the following way:

$$\left[Co_{Co}^{\bullet}\right] + 2\left(\left[V_{O3}^{\bullet\bullet}\right] + \left[V_{O2}^{\bullet\bullet}\right]\right) + z_A\left[A_{Lni}^{z_A\bullet}\right] = \left[Ba_{Ln2}^{/}\right] + \left[Co_{Co}^{/}\right] + z_B\left[B_{Co}^{z_B/}\right] \tag{S1}$$

with $A_{Lni}^{z_A\bullet}$ and $B_{Co}^{z_B/}$ denoting A- and B-site dopants while z_A and z_B standing for their effective charge numbers (0 or 1), respectively. Note, "Lni" index for A-site impurity indicates it can be introduced either in Ln-site (Ln1) or in Ba-site (Ln2) which is considered as fully substituted Ln2 position in the reference crystal chosen [4]. Accordingly, site balance conditions would be naturally changed accounting for the respective doping concentrations. Finally, the overall interrelations between concentrations of i-th component (placed in N(i) position with z_i effective charge) and temperature T in j-th quasichemical reaction would be established by the corresponding mass action law:

$$\prod_i \left[i_{N(i)}^{z_i} \right]^{\nu_{ij}} = \exp\left(\frac{\Delta S_j^0}{k_B} \right) \exp\left(\frac{-\Delta H_j^0}{k_B T} \right) \tag{S2}$$

where ν_{ij} denotes stoichiometric coefficient of i-th component, k_B – Boltzmann's constant and ΔS_j^0 with ΔH_j^0 are depicting the respective standard entropy/enthalpy changes in j-th reaction. Combining eqs. (S1), (S2) and site balance conditions one can obtain the following equations relating B-site defect concentrations to the overall oxygen stoichiometry in cobaltites considered:

$$\left[Co_{Co}^\times \right] = \frac{y + \sqrt{(x - y + 2\delta - 1)^2 - 4(x + 2\delta - 3)(x - 2y + 2\delta + 1)\exp\left(\frac{-\Delta H_{cd}^0}{k_B T} \right)} - 2}{4\exp\left(\frac{-\Delta H_{cd}^0}{k_B T} \right) - 1} \tag{S3}$$

$$\left[Co_{Co}^\bullet \right] = \frac{1}{2}\left(3 - \left[Co_{Co}^\times \right] \right) - \delta - \frac{x}{2} \tag{S4}$$

$$\left[Co_{Co}^/ \right] = \frac{1}{2}\left(1 - \left[Co_{Co}^\times \right] \right) + \delta + \frac{x}{2} - y \tag{S5}$$

with $x = z_A \left[A_{Lni}^{z_A \bullet} \right]$, $y = z_B \left[B_{Co}^{z_B /} \right]$ and ΔH_{cd}^0 depicting enthalpy change of reaction (4) in the main text of an article. Note, if z_A or z_B equal to 0, the respective contribution of x/y in (S1) will vanish. In this sense, x and y appearing in (S3) – (S5) are quite different from those presented in chemical formula. Accordingly, they would coincide only if 2+ and 3+ formal charges are ascribed to the respective dopants. Similarly, one can derive functional dependencies of O-sublattice defect concentrations; the most important for the present case are those for oxygen vacancies in O3 positions:

$$\left[V_{O3}^{\bullet\bullet} \right] = \frac{\delta}{2} - 2 + \frac{\sqrt{\left\{ \left(\exp\left(\frac{-\Delta H_{od}^0}{k_B T} \right) - 1 \right)(\delta - 4) - 3 \right\}^2 - 16\exp\left(\frac{-\Delta H_{od}^0}{k_B T} \right) - 5}}{2\left(\exp\left(\frac{-\Delta H_{od}^0}{k_B T} \right) - 1 \right)} \tag{S6}$$

where ΔH_{od}^0 is the enthalpy change for oxygen disordering (5) from the main text. With all defect concentrations specified one can relate equilibrium oxygen partial pressure (P_{O_2}) to inner stoichiometry of a particular cobaltite using mass action law for oxidation reaction (3):

$$\log\left(P_{O_2} \right) = 4\left\{ \log\frac{\left[Co_{Co}^/ \right]}{\left[Co_{Co}^\times \right]} + \log\sqrt{1 - \left[V_{O3}^{\bullet\bullet} \right]^{-1}} - \frac{\Delta H_{ox}^0}{2k_B T} + \frac{\Delta S_{ox}^0}{2k_B} \right\} \tag{S7}$$

which provides the desired linkage $\delta = f\left(T, P_{O_2}\right)$ if enthalpy ΔH_{ox}^0 and entropy ΔS_{ox}^0 of oxidation reaction (3) are known. The overall representation of eq. (S7) can be expanded so that to present P_{O2} as an explicit function of T and δ. After some algebra manipulations one can obtain:

$$P_{O_2} = \frac{K_{ox}^2 \left[\left[\left(\frac{\delta}{2} - 2 + \frac{\sqrt{\left\{\left(\exp\left(\frac{-\Delta H_{od}^0}{k_B T}\right) - 1\right)(\delta - 4) - 3\right\}^2 - 16\exp\left(\frac{-\Delta H_{od}^0}{k_B T}\right) - 5}}{2\left(\exp\left(\frac{-\Delta H_{od}^0}{k_B T}\right) - 1\right)}\right)^{-1}\right] - 1\right]^2}{\left[\frac{\left(4\exp\left(\frac{-\Delta H_{cd}^0}{k_B T}\right) - 1\right)\left(\frac{1}{2} + \delta + \frac{x}{2} - y\right)}{y + \sqrt{(x - y + 2\delta - 1)^2 - 4(x + 2\delta - 3)(x - 2y + 2\delta + 1)\exp\left(\frac{-\Delta H_{cd}^0}{k_B T}\right)} - 2} - \frac{1}{2}\right]^{-4}} \tag{S8}$$

with $K_{ox} = \exp\left(\frac{-\Delta S_{ox}^0}{k_B}\right)\exp\left(\frac{-\Delta H_{ox}^0}{k_B T}\right)$ denoting equilibrium constant of oxidation reaction. Accordingly, δ values can be obtained numerically from (S8) if all other parameters are known. Note, when applying charge neutrality (S1) to the studied $Pr_{1-x}Y_xBaCo_{2-y}Ni_yO_{6-\delta}$ materials one should consider $z_A = 0$ as Y is isovalent dopant to Pr while $z_B = 1$ suggesting Ni forms a $Ni_{Co}^{/}$ defect. For other cobaltites, i.e. $Gd_{0.8}La_{0.2}Ba_{1-x}La_xCo_2O_{6-\delta}$ one should use $z_A = 1$ due to Ba being replaced by La in the lattice.

S2. Conductivity model derivation

Both transport models proposed in the main text heavily rely on the fact that electrical conductivity σ can be summed up from partial contributions σ_i and thus transformed as:

$$\sigma = \sum_i \sigma_i = \left|\bar{e}\right|\left(N_p u_p + N_n u_n + N_e u_e\right) \tag{S9}$$

where $\bar{e}$ is absolute electrical charge, N_p, N_n and N_e denote volume concentrations of p-type, n-type and metallic-like charge carriers, respectively. These are well defined in the main text of an article: N_p term can be associated with Co^{4+} ions, N_n – with Co^{2+} and N_e – with Co^{3+} in HS state. Accordingly, these concentrations can be directly determined from defect chemistry model. Contrary to that, the expressions for mobility terms in eq. (S9) – u_p for holes, u_n for electrons and u_e for metallic subsystem are not so trivial. Below brief descriptions of what stands behind the formulated high temperature transport models used in this work are

outlined. For instance, if one is dealing with semiconducting type of polaron hopping transport the general idea of what is the mobility can be written as [5]:

$$\begin{bmatrix} hopping \\ mobility \end{bmatrix} = \begin{bmatrix} electrical \\ charge \end{bmatrix} \times \begin{bmatrix} hopping \\ frequency \end{bmatrix} \times \begin{bmatrix} hopping \\ probability \end{bmatrix} \qquad (S10)$$

Hence, an averaged movement of a particular carrier (i.e. polaron) through the lattice will be mostly influenced by the number of its attempts to overcome the potential barrier and the respective probability of successful transition. From a mathematical point of view polaron mobility for a k-th carrier is defined as [5]:

$$u_k = \frac{\left|\bar{e}\right| \nu_k^\# r_0^2 x_k}{k_B T} \exp\left(\frac{-E_k^\#}{k_B T}\right) \qquad (S11)$$

with $\nu_k^\#$ denoting hopping frequency, r_0 – polaron jump distance, x_k – mole fraction of sites available for a hop and $E_k^\#$ is energy barrier. One should note x_k term is introduced as the number of Co^{3+} sites which n- or p-type carriers can occupy. The respective quantities are well defined for both models considered in the main text of an article. To add, r_0 value can be simply approximated as pseudo-cubic unit cell parameter a_c of double perovskite structure. Consequently, assuming unit cell volume of $Pr_{1-x}Y_xBaCo_{2-y}Ni_yO_{6-\delta}$ solid solutions is $2a_c^3$ one can quickly arrive to a formulation of polaronic conductivity presented in the main text of an article.

When considering delocalized electronic transport one should use other principles in order to derive the mobility of the respective charge carriers. For instance, the corresponding formulation can be obtained in the framework of conventional band theory and generally reads as:

$$\begin{matrix} delocalized \\ carrier \\ mobility \end{matrix} = \frac{\begin{bmatrix} electrical \\ charge \end{bmatrix} \times \begin{bmatrix} relaxation \\ time \end{bmatrix} \times \begin{bmatrix} site \\ fraction \end{bmatrix}}{\begin{bmatrix} effective \\ mass \end{bmatrix}} \qquad (S12)$$

Therefore, a particular delocalized charge carrier moves freely from one collision to another with average collision rate related to relaxation time with an effective mass parameter determining the force acting on it. The principal difference in case of cobaltites studied is the presence of "site fraction" multiplier in formula (S12) which appears there due to spatial distribution of conduction channels. To be precise, some positions in crystal lattice in both models considered are participating in localized charge transport which implies they are to be

excluded from delocalized conduction pathways. As a result, the "classical" mobility term needs to be corrected. When applying this scheme to metallic subsystem one can arrive at the following expression for the mobility:

$$u_e = \frac{x_e \left| \overline{e} \right| \tau \big|_{E=E_F}}{m_e^*} \qquad (S13)$$

with E_F denoting Fermi energy, τ – relaxation time depending on energy E, m_e^* – effective mass and x_e is a site fraction term which equals unity for metallic component of conductivity (the number of carriers is uqual to the total amount of sites). At high temperature limit τ parameter can be reasonably approximated in a framework of acoustic scattering [6] which after some algebraic manipulations leads to the desired $u_e \sim T^{-1}$ law:

$$u_e = \frac{\left| \overline{e} \right| \tau_{0l}}{\sqrt{E_F} \left(m_e^* \right)^{5/2} T} \qquad (S14)$$

where τ_{0l} is a constant related to acoustic deformation potential in a crystal lattice [6]. Then, after several rearrangements the σ_e° parameter in eqs. (10) and (13) from the main text of an article could be expressed as a function of physical quantities – τ_{0l}, effective mass, Fermi energy:

$$\sigma_e^{\circ} = \frac{k_B \tau_{0l}}{\sqrt{E_F} \left(m_e^* \right)^{5/2} a_c^2} \qquad (S15)$$

Additional difficulties arise when delocalized p-type conduction is considered as in the case of model II. Then, general expression (S13) appears to be modified due to the necessity of averaging relaxation time with respect to energy thus transforming formula (S13) to:

$$u_p = \frac{x_h \left| \overline{e} \right| \langle \tau \rangle}{m_h^*} = \frac{4 x_h \left| \overline{e} \right|}{3 m_h^* \sqrt{\pi}} \int_0^{\infty} \tau \alpha^{3/2} \exp(-\alpha) d\alpha \qquad (S16)$$

with $\alpha = E/k_B T$, m_h^* - effective mass of a hole and x_h - a site fraction term. Note, parameter x_h introduced here does not equal unity because the amount of carriers is significantly less then the total amount of sites where they can appear (in case of model II these are Co^{3+} ions in IS states located in CoO_6 octahedra). Consequently, integrating eq. (S16) with relaxation time ascribed to acoustic scattering one can arrive to the expression presented below:

$$u_p = \frac{4|\bar{e}|\tau_{0l}\left[Co_{IS(\Diamond)}^{3+}\right]}{3\sqrt{k_B\pi}\left(m_h^*\right)^{5/2}T^{3/2}} = \frac{4|\bar{e}|\tau_{0l}(1-\delta)\left[Co^{3+}\right]}{3\sqrt{k_B\pi}\left(m_h^*\right)^{5/2}\left(1+\exp\left(\frac{-E_S}{k_BT}\right)\right)T^{3/2}} \quad (S17)$$

which after simple algebra manipulations can be used for evaluating parameter σ_p° presented in the main text:

$$\sigma_p^\circ = \frac{4\sqrt{k_B}\tau_{0l}}{3\sqrt{\pi}\left(m_h^*\right)^{5/2}a_c^2} \quad (S18)$$

As can be seen from expressions (S15) and (S18), both parameters σ_p° and σ_e° contain several quantities (effective mass, scattering parameter τ_{0l} etc.) which cannot be independently determined from fitting procedures. Consequently, it is convenient to use σ_p° and σ_e° as representative terms in conduction models discussed.

S3. Non-stoichiometry/conductivity data fitting results for different cobaltites

As discussed in the main text of an article, earlier published results on oxygen content and electrical conductivity for EBC, GBC and GLBC can be successfully described in a framework of theoretical model proposed. The respective fitting results are supplied within table S1.

Table S1. Thermodynamic and transport parameters obtained in the course of fitting experimental non-stoichiometry/conductivity data for different layered cobaltites

Parameter	Compound		
	EBC	GBC	GLBC
$\nu_n^{\#}$, s^{-1}	$(1.5 \pm 0.1)\times10^{13}$	$(1.7 \pm 0.13)\times10^{13}$	-
σ_p°, s^{-1}K$^{1/2}$	$(1.4 \pm 0.2)\times10^{15}$	$(1.75 \pm 0.2)\times10^{15}$	$(2.9 \pm 0.5)\times10^{15}$
σ_e°, s^{-1}	$(1.0 \pm 0.1)\times10^{14}$	$(5.0 \pm 1.0)\times10^{14}$	$(1.33 \pm 0.09)\times10^{14}$
E_n, kJ/mol	6.5 ± 0.8	6.3 ± 0.7	-
E_s, kJ/mol	7 ± 2	26 ± 3	5.5 ± 0.8
ΔH_{ox}^0, kJ/mol	-71 ± 4	-93 ± 3	-110 ± 3
ΔH_d^0, kJ/mol	12 ± 3	15 ± 4	41 ± 0.5
ΔH_{od}^0, kJ/mol	125 ± 2	112 ± 0.8	110 ± 15
ΔS_{ox}^0, J/mol/K	-67 ± 2	-89 ± 2	-70 ± 3

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