

Unusual enhancement of high-temperature electronic transport in PrBaCo₂O_{6-δ} at Ga doping: reasons and consequences

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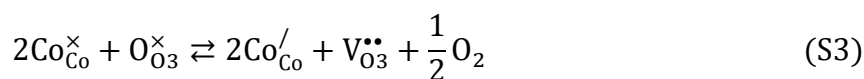
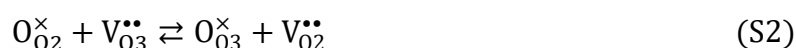
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SUPPLEMENTARY INFORMATION

S1. Defect chemistry model of PrBaCo_{2-x}Ga_xO_{6-δ} solid solutions

Layered cobaltites can be distinguished among other materials with exceedingly high concentrations of structural defects – vacancies, electron excitations etc. Recently, a mathematical model was developed for the description and interpretation of equilibrium among various defects and gaseous phase in PrBaCo_{2-x}Ga_xO_{6-δ} (PBCG) perovskite-like oxides. The essence of the model is based on Kröger–Vink formalism [1] with a PrCoO₃ reference crystal and Pr_{Pr}^x, Co_{Co}^x, O_{O1}^x, O_{O2}^x, O_{O3}^x regular sites. The oxygen sublattice appears to be divided because of the known inequivalence of the respective positions in layered cobaltites. Accordingly, Ba and Ga substitutions produce Ba_{Pr}[/] and Ga_{Co}^x defects, respectively. These are supposed to be unaffected by variations of temperature and gas atmosphere in the studied range of external conditions [1]. Other defects are considered to emerge from the following list of quasichemical reactions:



where Co_{Co}[•], Co_{Co}['], V_{O3}^{••} and V_{O2}^{••} denote electron hole, electron, oxygen vacancy in O3 and O2 positions, respectively. Applying mass action laws to eqs. (S1) – (S3) in ideal solution approximation and using charge neutrality/site balance conditions one can obtain a system of equations that can be solved to produce functional dependences of various defects on external parameters – temperature and partial pressure. Importantly, the incorporation of Ga modifies the defect equilibrium because some fraction of vacancies (ξ) appears to be excluded from the processes of exchange with the gas phase. These oxygen vacancies V_{Oi(excl)}^{••} are shown to be placed in the vicinity of Ga impurities thus forming GaO₄ tetrahedra in the lattice. The respective influence of the latter on PBCG defect structure can be presented as a reaction of vacancy trapping:



with the maximum amount of trapped vacancies assigned to ξ_{lim} value which can be computed using binomial distribution function [1]. Accordingly, various cobalt species' concentrations can be expressed as:

$$[Co_{Co}^{\bullet}] = \frac{3-x}{2} + \frac{1 - \sqrt{\left(1 - K_{cd}^{\circ} e^{-\frac{\Delta H_{cd}^{\circ}}{RT}}\right) (2\delta - x + 1)(2\delta + x - 3) + (x - 2)^2 - \frac{x}{2}}}{\left(K_{cd}^{\circ} e^{-\frac{\Delta H_{cd}^{\circ}}{RT}} - 1\right)} - \delta \quad (\text{S5})$$

$$[Co_{Co}^{\times}] = \frac{x + \sqrt{4\left(1 - K_{cd}^{\circ} e^{-\frac{\Delta H_{cd}^{\circ}}{RT}}\right) (2\delta - x + 1)(2\delta + x - 3) + 4(x - 2)^2 - 2}}{\left(K_{cd}^{\circ} e^{-\frac{\Delta H_{cd}^{\circ}}{RT}} - 1\right)} - \frac{x}{2} \quad (\text{S6})$$

$$[Co'_{Co}] = \frac{1-x}{2} + \frac{1 - \sqrt{\left(1 - K_{cd}^{\circ} e^{-\frac{\Delta H_{cd}^{\circ}}{RT}}\right) (2\delta - x + 1)(2\delta + x - 3) + (x - 2)^2 - \frac{x}{2}}}{\left(K_{cd}^{\circ} e^{-\frac{\Delta H_{cd}^{\circ}}{RT}} - 1\right)} + \delta \quad (\text{S7})$$

while the overall model equation establishing linkage between oxygen partial pressure, non-stoichiometry and temperature can be formulated as:

$$P_{O_2} = \frac{e^{-\frac{2(\Delta G_{ox}^{\circ} - \Delta H_{od}^{\circ})}{RT}} \left\{ (2\delta - 1) \left(\frac{3-x}{2} + \frac{1 - \sqrt{\left(1 - e^{-\frac{\Delta H_{cd}^{\circ}}{RT}}\right) (2\delta - x + 1)(2\delta + x - 3) + (x - 2)^2 - \frac{x}{2}}}{\left(e^{-\frac{\Delta H_{cd}^{\circ}}{RT}} - 1\right)} - \delta \right)^{-1} + 1 \right\}^4}{\left\{ (1 - \xi) \left(\frac{\delta - \xi}{2} + \frac{2\xi + \sqrt{\left[(4 + \xi - \delta) \left(e^{-\frac{\Delta H_{pd}^{\circ}}{RT}} - 1 \right) + 2\xi - 5 \right]^2 + 4(1 - \xi)(2\xi - \delta) \left(e^{-\frac{\Delta H_{pd}^{\circ}}{RT}} - 1 \right) - 5}}{2 \left(e^{-\frac{\Delta H_{pd}^{\circ}}{RT}} - 1 \right)} - 2 \right)^{-1} - 1 \right\}^{-2}} \quad (\text{S8})$$

with $\Delta G_{ox}^{\circ} = \Delta H_{ox}^{\circ} - T\Delta S_{ox}^{\circ}$ denoting Gibbs free energy of reaction (S3), ΔH_{cd}° and ΔH_{od}° designating enthalpy changes for reactions (S1) and (S2), respectively. In its turn, the fraction of trapped vacancies ξ is determined via the following relation:

$$\xi = \frac{\xi_{\text{lim}}}{\left(K_{Ex}^{\circ} e^{\frac{\Delta H_{Ex}^{\circ}}{RT}} + 1 \right)} \quad (\text{S9})$$

where ΔH_{Ex}° and K_{Ex}° are thermodynamic parameters of reaction (S4). Their numerical values were previously determined in [...]. It should be stressed the model discussed was earlier used to successfully interpret thermodynamic dependences of oxygen content in PBCG on temperature and oxygen chemical potential changes (which can be trivially converted to partial pressure P_{O_2}). However, it was supposed that the entropy contribution in reactions (S1) and (S2) is non-negligible, while further reports indicated this proposition is not entirely correct [2]. Therefore, in

order to properly assess defect concentrations we've used eqs. (S5) – (S8) with fixed to 0 entropies of reactions without oxygen exchange.

S2. Conductivity model of $\text{PrBaCo}_{2-x}\text{Ga}_x\text{O}_{6-\delta}$ solid solutions

Layered cobaltites studied were previously shown to possess quasi-2D character of electronic conductivity with two main channels of current conduction – the metallic one and the semiconducting one [3]. The former is attributed to Co^{3+} ions ($\text{Co}_{\text{Co}}^{\times}$ in the scope of defect chemistry) resting in oxygen octahedra and possessing high total spin values. The latter is linked with Co^{2+} and Co^{4+} ions acting as localized electrons (polarons) and delocalized electron holes, respectively (these are $\text{Co}_{\text{Co}}^{\bullet}$ and $\text{Co}_{\text{Co}}^{\prime}$ in Kröger–Vink formalism). Total conductivity σ can be formulated as a sum of the aforementioned individual components [3]:

$$\sigma = \sigma_e + \sigma_p + \sigma_n \quad (\text{S10})$$

where σ_e represents metallic conductivity, σ_p – p-type and σ_n – n-type conductivities, respectively. Each carrier in this model is described with several parameters – the metallic subsystem relies on σ_e° term which reflects the mobility of the respective charge carriers. P-type conductivity is presented by similar parameter σ_p° . Another important value is the energy of spin splitting E_S , which governs the distribution of Co^{3+} spin states in octahedral oxygen coordination. In their turn, n-type polaronic carriers are distinguished with a hopping frequency $\nu_n^{\#}$ and hopping energy E_n . Carrier concentrations are ascribed to equilibrium defect concentrations discussed in previous section. Accordingly, one can write down particular expressions for each contribution to total conductivity:

$$\sigma_e = \frac{N_A |\bar{e}|^2 [\text{Co}_{\text{Co}}^{\times}] \sigma_e^{\circ}}{3aRT} \left(\frac{1 - \delta}{1 + \exp\left(\frac{E_S}{RT}\right)} \right) \quad (\text{S11})$$

$$\sigma_p = \frac{N_A |\bar{e}|^2 [\text{Co}_{\text{Co}}^{\times}] [\text{Co}_{\text{Co}}^{\bullet}] \sigma_p^{\circ}}{3aRT^{3/2}} \left(\frac{1 - \delta}{1 + \exp\left(\frac{-E_S}{RT}\right)} \right) \quad (\text{S12})$$

$$\sigma_n = \frac{N_A |\bar{e}|^2 \nu_n^{\#} \delta [\text{Co}_{\text{Co}}^{\times}] [\text{Co}_{\text{Co}}^{\prime}]}{3aRT} \exp\left(\frac{-E_n}{RT}\right) \quad (\text{S13})$$

Further details of model formulation can be found elsewhere [3]. Applying this model to PBCG faces a particular difficulty due to the essential basis led in the foundation of the equations used. Namely, it is supposed that oxygen vacancies in O2 positions below $\delta < 1$ values can be

disregarded [3] as they interrupt oxygen-cobalt chains that serve as conducting channels for n-type carriers. As can be seen from the previous section this hypothesis is not completely valid for PBCG at high temperatures because of ξ parameter. Indeed, GaO_4 tetrahedra formed in the lattice partly disrupt the aforementioned chains as they trap O2 vacancies placed nearby and can therefore influence on n-type conductivity. However, the respective contribution in case of PBCG can be easily implemented into the model equations. One should consider, that, at first approximation, Co-O-Ga bonds can be randomly distributed across the lattice. Then, the averaged fraction of trapped O2 vacancies in the direction of current flow would be equal half of that presented in the crystal. Hence, it is reasonable to exclude those sites from the total amount of available sites for electron hopping in the final expression for σ_n . This correction can be made as:

$$\frac{\text{Amount of available positions}}{\text{of O2 positions}} = \left(\frac{\text{total amount of O2 positions} - \text{half of trapped O2 positions}}{\text{total amount of O2 positions}} \right) \times \left(\text{Number of Co}^{3+} \text{ ions in pyramids} \right) \quad (\text{S14})$$

Accordingly, total amount of O2 positions in PBCG is 4 and hence the desired value would equal $\delta[\text{Co}_{\text{Co}}^{\times}] \left(1 - \frac{\xi}{8}\right)$. Further implementation of this clarifying additive is trivial and can be done following the general derivation of the model considered [3].

References

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