J Mater Sci (2007) 42:1909–1914
DOI 10.1007/s10853-006-0346-7

NONSTOICHIOMETRIC COMPOUNDS

Defect structure and charge transfer in undoped and doped lanthanum cobaltites

**A. N. Petrov · A. Yu. Zuev · A. I. Vylkov ·
D. S. Tsvetkov**

Received: 30 November 2005 / Accepted: 17 April 2006 /

Abstract The results of electronic conductivity and Seebeck coefficient are presented for perovskite-type undoped cobaltite $LaCoO_{3-\delta}$, doped with strontium $La_{0.7}Sr_{0.3}CoO_{3-\delta}$, and doped with copper $LaCo_{0.7}Cu_{0.3}O_{3-\delta}$. The electronic conductivity and the Seebeck coefficient were studied as a function of pO_2 in the range $10^{-6} \le pO_2/\mathrm{atm} \le 1$ at temperatures between 1073 and 1323 K. The charge transfer mechanism in the oxides studied is revealed within the framework of localized charge carriers approach on the basis of the defect structure modeling. $LaCoO_{3-\delta}$ and $La_{0.7}Sr_{0.3}CoO_{3-\delta}$ are shown to be the typical small polaron hopping conductors with p-type small polarons at Co sites, $\mathrm{Co}_{\mathrm{Co}}^{\bullet}$, as major carriers and n-type small polarons, $\mathrm{Co}_{\mathrm{Co}}^{/}$, as minor carriers in the temperature range investigated. The charge transfer in copper-doped cobaltite $LaCo_{0.7}Cu_{0.3}O_{3-\delta}$ seems to be carried out by means both hopping of n-type small polarons, $\mathrm{Cu}_{\mathrm{Co}}^{/}$ and $\mathrm{Co}_{\mathrm{Co}}^{/}$, at copper and cobalt sites, respectively, and p-type small polarons at Co sites. The mobilities and nonconfigurational entropies of charge transfer are determined for all types of charge carriers.

Introduction

Perovskite-type doped lanthanum cobaltites $La_{1-x}A_xCo_{1-z}B_zO_{3-\delta}$, where A is an alkaline-earth metal and B is a 3d-metal, have received great attention as electrode and membrane materials for high temperature electrochemical devices due to their high oxygen-ionic and electronic conductivity. There have been many attempts to interpret the unique transport properties of $La_{1-x}A_x{'}CoO_{3-\delta}$ ($A' = $ Ca and Sr) [1–7] and $LaCo_{1-y}B_y{'}O_{3-\delta}$ ($B' = $ Fe, Ni, and Cu) [8, 9], involving various conduction mechanisms and a variety of defect species and cobalt spin states. Raccah and Goodenough [7] first proposed a first-order localized-to-itinerant electron transition at 1210 K based upon electrical measurements and differential thermal analysis (DTA) results. Thornton et al. [10] attributed the DTA results of Goodenough [7] to presence of CoO as an impurity phase in the sample. They suggested [10] a gradual transition involving the thermal promotion of electrons from π^* band associated with the localized t_{2g} orbitals to the delocalized σ^* band associated with the e_g orbitals. Later Goodenough et al. [11] proposed an evolutional localized-to-itinerant electron transition based on the presence of Co in different spin states, instead of a phase transition, in order to explain the magnetic and transport properties of lanthanum cobaltite-based oxides. This model did not account, however, the possibility of Co disproportionation consisting in the transfer of an electron between adjacent Co^{3+} ions and resulting in an population of Co^{2+} and Co^{4+} ions. Contrary, Sehlin et al. [6] explained the Seebeck coefficient and effective paramagnetic moments for $LaCoO_{3-\delta}$ on the basis of a semiempirical model involving the mechanism of charge disproportionation in the Co sublattice. Later Kozhevnikov et al. [12] applied the model mentioned above to interpret the electronic conductivity and Seebeck coefficient of $La_{0.7}Sr_{0.3}CoO_{3-\delta}$. They first

---

A. N. Petrov · A. Yu. Zuev (✉) · A. I. Vylkov ·
D. S. Tsvetkov
Chemical Department, Ural State University, Lenin Av. 51,
620083 Yekaterinburg, Russia
e-mail: andrew.zuev@usu.ru

described the nature of electronic transport in $La_{0.7}Sr_{0.3}CoO_{3-\delta}$ on the basis of joint analysis of the data on the oxygen nonstoichiometry, electronic conductivity, and Seebeck coefficient as functions of oxygen partial pressure.

Thus, despite intense activity and continuous interest over the past decades, the electronic structure and the mechanism of conductivity in undoped and doped lanthanum cobaltites remain a controversial topic of discussion.

So far, the researchers [1, 10, 11, 13, 14] have primarily interpreted the magnetic and transport properties of these cobaltites in terms of a transition from localized-to-itinerant electron state, focusing upon the presence of Co atoms in different spin states within the framework of band theory. This physical approach has a lot of problems regarding the definition of energy levels of 3d-atoms and oxygen, which in turn depend on crystal field, a degree of localization of conductive electronic species. However, there is an alternative approach within the framework of which the basic statements of a physical approach is supplemented by a thermodynamic description of equilibrium atomic and electronic defects [3, 4, 6, 9, 12]. The defect chemistry of undoped and doped lanthanum cobaltites is not completely clarified. The defect structure of these perovskite-type oxides is enough complicated and depends on a nature and a place of dopants, oxygen nonstoichiometry, temperature and oxygen partial pressure. Therefore, the priority goal of the present study was to reveal the nature of a charge transfer in undoped $LaCoO_{3-\delta}$, doped with Sr on A site $La_{0.7}Sr_{0.3}CoO_{3-\delta}$, and doped with Cu on B site $LaCo_{0.7}Cu_{0.3}O_{3-\delta}$ on the basis of joint analysis of the data on the oxygen nonstoichiometry $\delta = f(T, pO_2)$, electronic conductivity $\sigma = \varphi(T, pO_2, \delta)$, and Seebeck coefficient $Q_z = F(T, pO_2, \delta)$. Some preliminary results were reported by us in a recent paper [9]. The defect structure of all cobaltites mentioned above have been discussed in our previous work [15].

Experimental

The powder samples were prepared using a standard ceramic technique as described in works [4, 9]. The samples were identified by X-ray powder diffraction as single perovskite-type phases. Ceramic samples with densities of about 93% of the theoretical value were obtained by sintering of the axially pressed powders at temperatures between 1200 and 1400°C in air. Specimens were annealed at the sintering temperature for 20 h and then slowly cooled down to the room temperature. The electrical conductivity (σ, $S \cdot cm^{-1}$) of so-prepared samples was measured by means of standard four-probe *dc* technique. The Seebeck coefficient was measured according to a technique given elsewhere [9, 12]. The measured values of Seebeck coefficient of the sample were corrected taking into account those for Pt leads. The electrical conductivity σ and Seebeck coefficient Q of $LaCoO_{3-\delta}$, $La_{0.7}Sr_{0.3}CoO_3$ [12], and $LaCo_{0.7}Cu_{0.3}O_3$, measured at different temperatures, are plotted versus oxygen partial pressure in Figs. 1, 2, and 3, respectively. As can be seen all oxides investigated have a metallic p-type conductivity, since the values of Seebeck coefficient are positive and conductivity decreases with increasing of temperature.

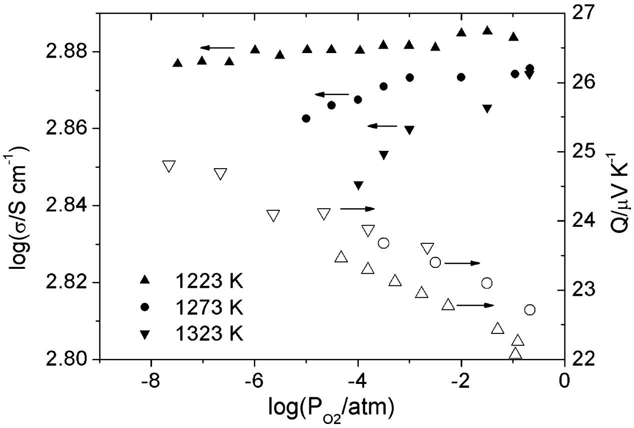

Fig. 1 The conductivity (filled symbols) and Seebeck coefficient (open symbols) of undoped $LaCoO_{3-\delta}$ depending on oxygen partial pressure at different temperatures

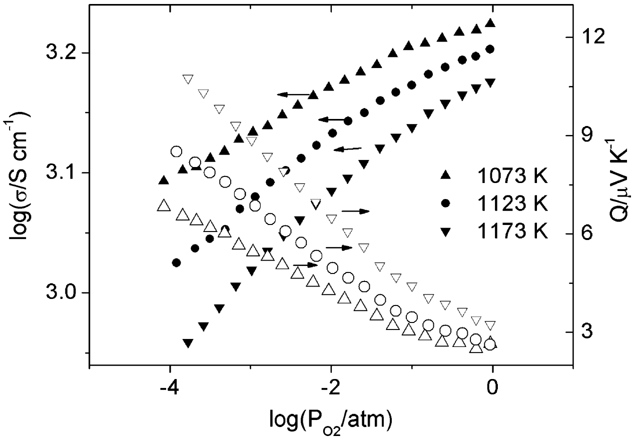

Fig. 2 The conductivity (filled symbols) and Seebeck coefficient (open symbols) of Sr-doped $La_{0.7}Sr_{0.3}CoO_{3-\delta}$ [12] depending on oxygen partial pressure at different temperatures

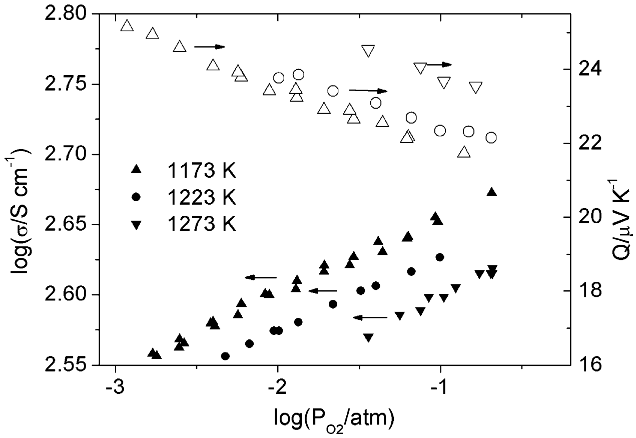

Fig. 3 The conductivity (filled symbols) and Seebeck coefficient (open symbols) of Cu-doped $LaCo_{0.7}Cu_{0.3}O_{3-\delta}$ depending on oxygen partial pressure at different temperatures

Results and discussion

The electrical conductivity σ and Seebeck coefficient Q of lanthanum cobaltites investigated are very sensitive to oxygen nonstoichiometry δ. The isothermal dependences of the electrical conductivity σ and Seebeck coefficient Q have been treated using the phase diagram $\delta - \log(P_{O_2}) - T$, presented in our previous paper [15]. The results of the experimental data treatment are shown in Figs. 4, 5 and 6. As follows from these figures the conductivity decreases apparently and Seebeck coefficient increases with increasing of oxygen nonstoichiometry in the oxides. As seen dependences $\log(\sigma_T) - \delta$ and $Q_T - \delta$ are linearized very well.

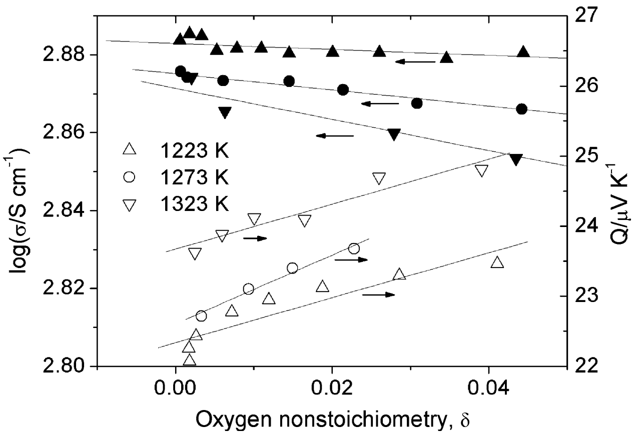

Fig. 4 The conductivity (filled symbols) and Seebeck coefficient (open symbols) of undoped $LaCoO_{3-\delta}$ depending on the oxygen nonstoichiometry at different temperatures

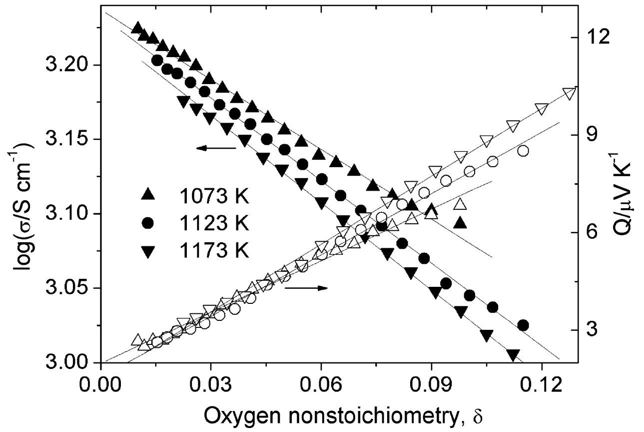

Fig. 5 The conductivity (filled symbols) and Seebeck coefficient (open symbols) of Sr-doped $La_{0.7}Sr_{0.3}CoO_{3-\delta}$ [12] depending on the oxygen nonstoichiometry at different temperatures

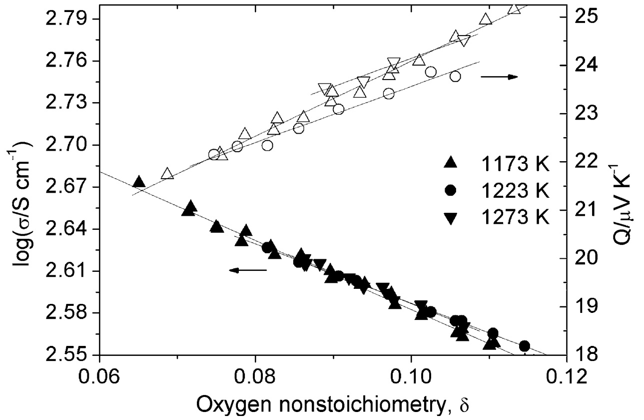

Fig. 6 The conductivity (filled symbols) and Seebeck coefficient (open symbols) of Cu-doped $LaCo_{0.7}Cu_{0.3}O_{3-\delta}$ depending on the oxygen nonstoichiometry at different temperatures

In the previous paper [15] defect species $\mathrm{Co}_{\mathrm{Co}}^{\bullet}$ (or $h^{\bullet}$), $\mathrm{Co}_{\mathrm{Co}}^{/}$ (or $e^{/}$), $\mathrm{V}_{\mathrm{O}}^{\bullet\bullet}$, $\mathrm{Sr}_{\mathrm{La}}^{/}$, and $\mathrm{Cu}_{\mathrm{Co}}^{/}$ (all written using standard Kroeger–Vink notation) were found to be the predominant defects in the lattice of undoped and Sr-or Cu-doped lanthanum cobaltites. Within the framework of localized electronic defects model disproportionation of cobalt

$$2\mathrm{Co}_{\mathrm{Co}}^{\times} = \mathrm{Co}_{\mathrm{Co}}^{/} + \mathrm{Co}_{\mathrm{Co}}^{\bullet} \tag{1}$$

was shown to be predominant reaction of charge carriers in the undoped lanthanum cobaltite.

In copper doped $LaCo_{0.7}Cu_{0.3}O_3$ the following reaction can proceed as well:

$$\mathrm{Cu}_{\mathrm{Co}}^{\times} + \mathrm{Co}_{\mathrm{Co}}^{\times} = \mathrm{Cu}_{\mathrm{Co}}^{/} + \mathrm{Co}_{\mathrm{Co}}^{\bullet}, \tag{2}$$

where $\mathrm{Co}_{\mathrm{Co}}^{\bullet}$ is the hole trapped on Co site; $\mathrm{Co}_{\mathrm{Co}}^{/}$ and $\mathrm{Cu}_{\mathrm{Co}}^{/}$ are the electrons trapped on Co and Cu ions, respectively. The equilibrium constants of the reactions of predominant defects formation were fitted as functions of temperature and, therefore, concentration of all defect species was calculated as a function of δ, $p\mathrm{O}_2$ and temperature for undoped $\mathrm{LaCoO}_{3-\delta}$ and acceptor doped $\mathrm{La}_{0.7}\mathrm{Sr}_{0.3}\mathrm{CoO}_3$ and $\mathrm{LaCo}_{0.7}\mathrm{Cu}_{0.3}\mathrm{O}_3$ lanthanum cobaltites [15]. The data on conductivity and thermoelectrical power show that electronic holes are the most mobile charge carriers, whereas electrons seem to be less mobile, and double charged oxygen vacancies $\mathrm{V}_{\mathrm{O}}^{\bullet\bullet}$ are the least mobile in $\mathrm{LaCoO}_{3-\delta}$ in temperature range investigated. Transport number of oxygen vacancies is negligible and, therefore, the total electrical conductivity of these oxides is given by the equation

$$\sigma = \frac{a \cdot |e|}{V_a}(v_e n + v_h p), \tag{3}$$

where V_a is the volume of unit cell in a hexagonal symmetry; a is the number of formula units per unit cell and equals to 6; e is the charge of electron; n and p have their common meaning; v_h and v_e, are the mobilities of holes and electrons, respectively. If electrons and holes are treated as localized on cobalt sites, then n and p should be substituted by $[\mathrm{Co}_{\mathrm{Co}}^{/}]$ and $[\mathrm{Co}_{\mathrm{Co}}^{\bullet}]$.

The Seebeck coefficient of the oxides is a function of the concentration of all charge carriers

$$Q = t_e Q_e + t_h Q_h = \frac{n \cdot Q_e + L \cdot p \cdot Q_h}{n + L \cdot p}, \tag{4}$$

where Q_h and Q_e are partial thermoelectric coefficients; t_h and t_e are transport numbers of holes and electrons, respectively; $L = v_h/v_e$ is the ratio of the mobilities. In the model of localized carriers Q_h and Q_e are given by Heikes formula [16]

$$\begin{aligned} Q_h &= \frac{k}{|e|}\left[\ln\left\{\frac{1}{\beta_h}\frac{1-[\mathrm{Co}_{\mathrm{Co}}^{\bullet}]}{[\mathrm{Co}_{\mathrm{Co}}^{\bullet}]}\right\} + \frac{S_h^*}{k}\right], \\ Q_e &= -\frac{k}{|e|}\left[\ln\left\{\beta_e\frac{1-\left[\mathrm{Co}_{\mathrm{Co}}^{/}\right]}{\left[\mathrm{Co}_{\mathrm{Co}}^{/}\right]}\right\} + \frac{S_e^*}{k}\right], \end{aligned} \tag{5}$$

where $\beta_h = \frac{5}{6}$ and $\beta_e = \frac{4}{5}$ are the spin degenerate factors for cobalt ions $\mathrm{Co}^{\mathrm{IV}}$ and $\mathrm{Co}^{\mathrm{II}}$, respectively [13]; k is the Boltzmann constant; $S_{h/e}^* = \frac{H_{h/e}^*}{T}$ is the entropy and $H_{h/e}^*$ is the enthalpy of transfer of holes and electrons, respectively. Entropy term $\frac{S_{h/e}^*}{e}$, which is usually lower than 10 μV/K [14], is often neglected in comparison with configurational term $\frac{k}{|e|}\left[\ln\left\{\frac{1-[\mathrm{Co}_{\mathrm{Co}}^{\bullet}]}{[\mathrm{Co}_{\mathrm{Co}}^{\bullet}]}\right\}\right]$ for localized electron defects [16]. Equations (3) and (4) contain charge carriers concentrations determined in our previous paper [15] and mobilities of electrons v_e and holes v_h, which are a priori unknown. Simultaneous analysis of Eqs. (3) and (4), and experimental values of σ and Q at given T and δ allows to determine the unknown parameters v_e, (or v_h), L by solving the following set of equations:

$$\left.\begin{aligned} \sigma_{(T,\delta=\mathrm{Const})} &= \frac{a \cdot e}{V_a} \cdot v_e\left(L \cdot p_{T,\delta} + n_{T,\delta}\right) \\ Q_{(T,\delta=\mathrm{Const})} &= \frac{n_{T,\delta}Q_e + L \cdot p_{T,\delta}Q_h}{L \cdot p_{T,\delta} + n_{T,\delta}} \end{aligned}\right\}. \tag{6}$$

Charge transfer in the oxides studied in this work is usually explained by hopping mechanism or in terms of localized charges [1, 5, 6]. From the beginning, therefore, partial thermoelectric coefficients were estimated using the polaron theory. For solving the set Eq. (6) the entropy term $S_{h/e}^*$ was assumed to be negligible, that is $S_{h/e}^* = \frac{H_{h/e}^*}{T} \approx 0$. Results obtained in this way are summarized in Table 1. As can be seen large scattering is observed for the values of calculated mobilities at relatively low temperatures. Moreover, this scattering seems to depend on oxygen nonstoichiometry. Scattering of calculated values decreases at high temperatures. In Sr-doped lanthanum cobaltite $\mathrm{La}_{0.7}\mathrm{Sr}_{0.3}\mathrm{CoO}_{3-\delta}$ mobility of hole $\mathrm{Co}_{\mathrm{Co}}^{\bullet}$ is lower than that of electron $\mathrm{Co}_{\mathrm{Co}}^{/}$.

Afterwards more precise correlation analysis of the isothermal dependencies $Q_T = f(\delta)_T$ was carried out taking into account entropy term $\frac{S_{h/e}^*}{e}$ according to Eq. (5). Substitution of expression Eq. (5) in expression Eq. (4) leads to the following equation

$$Q_T = \frac{\frac{k}{e} \cdot \left[L \cdot p \cdot \ln\left(\frac{6\cdot(1-p)}{5\cdot p}\right) + \frac{S_h}{k}\right] - \frac{k}{e} \cdot \left[n \cdot \ln\left(\frac{4\cdot(1-n)}{5\cdot n}\right) + \frac{S_e}{k}\right]}{L \cdot p + n}. \tag{7}$$

where $p = p(\delta) = \left[\mathrm{Co}_{\mathrm{Co}}^{\bullet}\right]$, $n = n(\delta) = \left[\mathrm{Co}_{\mathrm{Co}}^{/}\right]$(or $n = n(\delta) = \left[\mathrm{Co}_{\mathrm{Co}}^{/}\right] + \left[\mathrm{Cu}_{\mathrm{Co}}^{/}\right]$ for $\mathrm{LaCo}_{0.7}\mathrm{Cu}_{0.3}\mathrm{O}_3$) are the functions of oxygen nonstoichiometry computed on the basis of the model of delocalized charge carriers [15]. Calculated as mentioned above mobilities ratio L was then fixed and nonconfigurational term $\frac{S_{h/e}^*}{e}$ was varied at first. Then mobilities ratio L was varied to reduce a standard deviation. Results obtained in this way are summarized in Table 2. Figure 7 shows the experimental data and theoretical dependencies of Seebeck coefficient of the oxides investigated on

Table 1 Results of charge carriers mobility calculations

T, K	δ	*L*	ν_e, cm$^2\cdot$ V$^{-1}\cdot$ c^{-1}	ν_h, cm$^2\cdot$ V$^{-1}\cdot$ c^{-1}
$LaCoO_{3-\delta}$				
1223	0.01	1.388	2.512	3.488
1223	0.02	1.837	2.179	4.004
1223	0.03	2.386	1.906	4.549
1223	0.04	3.031	1.685	5.106
1273	0.01	1.162	1.142	1.327
1273	0.02	1.276	1.086	1.385
1273	0.03	1.399	1.032	1.444
1273	0.04	1.532	0.982	1.504
1323	0.02	1.140	0.592	0.675
1323	0.03	1.155	0.583	0.673
1323	0.04	1.169	0.574	0.671
$La_{0.7}Sr_{0.3}CoO_{3-\delta}$				
1073	0.02	0.065	27.136	1.763
1073	0.04	0.081	22.942	1.850
1073	0.06	0.105	18.883	1.982
1073	0.08	0.145	15.057	2.183
1073	0.1	0.217	11.526	2.498
1123	0.02	0.111	15.021	1.664
1123	0.04	0.135	12.603	1.705
1123	0.06	0.172	10.337	1.777
1123	0.08	0.229	8.270	1.890
1123	0.1	0.321	6.431	2.062
1173	0.02	0.175	8.881	1.554
1173	0.04	0.209	7.490	1.566
1173	0.06	0.257	6.202	1.596
1173	0.08	0.327	5.044	1.649
1173	0.1	0.429	4.029	1.729
$LaCo_{0.7}Cu_{0.3}O_{3-\delta}$				
1173	0.07	14.410	0.850	12.254
1173	0.08	18.213	0.728	13.252
1173	0.09	22.573	0.629	14.197
1173	0.1	27.421	0.548	15.030
1223	0.08	12.261	0.704	8.632
1223	0.09	14.953	0.616	9.211
1223	0.1	17.973	0.543	9.761
1273	0.08	8.703	0.685	5.958
1273	0.09	10.460	0.600	6.277
1273	0.1	12.406	0.529	6.568

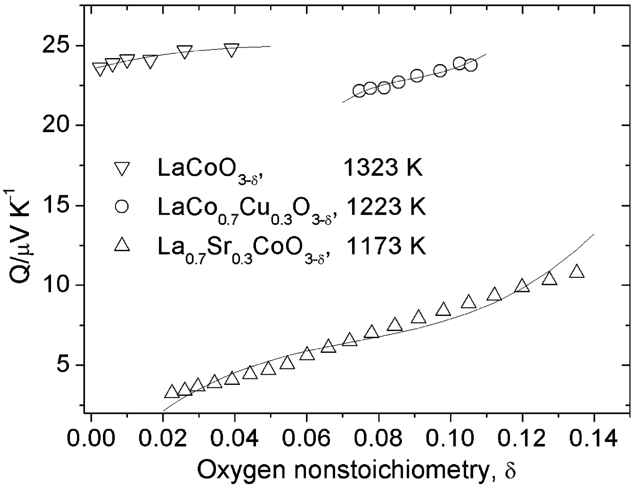

Fig. 7 Fitted curves results for Seebeck coefficient of the lanthanum cobaltites studied according to Eq. (7) at selected temperatures

oxygen nonstoichiometry. As seen the model Eq. (7) fits experimental data very well at selected temperatures over complete oxygen nonstoichiometry range investigated. Small negative values of entropy term $\frac{S^*_{h/e}}{e}$ (see Table 2) can be explained by partial failure of random distribution of charged defects due to the electron or/and hole trapping with the formation of possible associates $\left(V_O^{\bullet\bullet}Co_{Co}^{/}\right)^{\bullet}$, $\left(Sr_{La}^{/}Co_{Co}^{\bullet}\right)^{\times}$ and $\left(Cu_{Co}^{/}Co_{Co}^{\bullet}\right)^{\times}$. Nonconfigurational term of entropy $\frac{S^*_{h/e}}{e}$ has the lowest value for $LaCoO_{3-\delta}$ and decreases with increase temperature for all samples. Contribution of this value to overall Seebeck coefficient is enough small and do not exceed the value of 0.05%, 0.05%, and 0.1 % for $LaCoO_{3-\delta}$, $La_{0.7}Sr_{0.3}CoO_{3-\delta}$, and $LaCo_{0.7}Cu_{0.3}O_{3-\delta}$, respectively.

Thus, the quantitative analysis of a charge transfer in the undoped $LaCoO_{3-\delta}$, acceptor doped $La_{0.7}Sr_{0.3}CoO_{3-\delta}$ and $LaCo_{0.7}Cu_{0.3}O_{3-\delta}$ lanthanum cobaltites was carried out on the basis of the localized electronic species model. The mobilities of localized charge carriers were determined and a nonconfigurational term of entropy was estimated for all oxides studied.

Table 2 Results of nonlinear fit of Seebeck coefficient according to Eq. (7)

	L	*Se*, eV K^{-1}	*Sh*, eV K^{-1}
		$LaCoO_{3-\delta}$	
1273	1.701 (±0.083)	–6.93E–5 (±3E–6)	–1.078E–4 (±1.7E–6)
1323	3.240 (±0,192)	7.41E–5 (±7.7E–6)	–5.00E–5 (±1.1E–6)
		$La_{0.7}Sr_{0.3}CoO_{3-\delta}$	
1073	0.962 (±0.075)	–2.44E–4 (±2.4E–5)	1.64E–4 (±2.2E–5)
1123	1.008 (±0.051)	–1.91E–4 (±2.8E–5)	1.48E–4 (±2.5E–5)
1173	1.091 (±0.055)	–1.45E–4 (±2.8E–5)	1.24E–4 (±2.4E–5)
		$LaCo_{0.7}Cu_{0.3}O_{3-\delta}$	
1173	51.896 (±1.813)	–6.7E–5 (±4.2E–6)	–4.12E–4 (±7.1E–5)
1223	33.395 (±2.708)	–6.37E–5 (±8.2E–6)	–3.71E–4 (±1.6E–5)
1273	26.202 (±6.607)	–5.63E–5 (±2.4E–6)	–3.43E–4 (±4.7E–5)

Values of entropies are given per one charge carrier

Conclusions

The electronic conductivity and the Seebeck coefficient of $\mathrm{LaCoO_{3-\delta}}$, $\mathrm{La_{0.7}Sr_{0.3}CoO_{3-\delta}}$, and $\mathrm{LaCo_{0.7}Cu_{0.3}O_{3-\delta}}$ were studied as a function of $p\mathrm{O_2}$ in the range $10^{-6} \le p\mathrm{O_2}/\mathrm{atm} \le 1$ at temperatures between 1073 and 1323 K. The charge transfer mechanism in the oxides studied was revealed within the framework of localized charge carriers approach using results of defect structure modeling performed by us in the previous work [15]. $\mathrm{LaCoO_{3-\delta}}$ and $\mathrm{La_{0.7}Sr_{0.3}CoO_{3-\delta}}$ were shown to be the typical small polaron hopping conductors with p-type small polarons at Co sites, $\mathrm{Co}_{\mathrm{Co}}^{\bullet}$, as major carriers and n-type small polarons, $\mathrm{Co}_{\mathrm{Co}}^{/}$, as minor carriers in the temperature range investigated. The charge transfer in copper-doped cobaltite $\mathrm{LaCo_{0.7}Cu_{0.3}O_{3-\delta}}$ seems to be carried out by means both hopping of n-type small polarons, $\mathrm{Cu}_{\mathrm{Co}}^{/}$ and $\mathrm{Co}_{\mathrm{Co}}^{/}$, at copper and cobalt sites, respectively, and p-type small polarons at Co sites. The mobilities and nonconfigurational entropies of charge transfer are determined for all types of charge carriers. Small negative values of entropy term $\frac{S^{*}_{h/e}}{e}$ can be explained by partial failure of random distribution of charged defects due to the electron or/and hole trapping with the formation of possible associates $\left(\mathrm{V}_{\mathrm{O}}^{\bullet\bullet}\mathrm{Co}_{\mathrm{Co}}^{/}\right)^{\bullet}$, $\left(\mathrm{Sr}_{\mathrm{La}}^{/}\mathrm{Co}_{\mathrm{Co}}^{\bullet}\right)^{\times}$, and $\left(\mathrm{Cu}_{\mathrm{Co}}^{/}\mathrm{Co}_{\mathrm{Co}}^{\bullet}\right)^{\times}$.

Acknowledgements This work was supported by the Russian Foundation for Basic Research grants Nos. 04-03-32142 and 06-08-08120, the US Civilian Research & Development Foundation (project REC-005) and the Ministry of Education (grant no. A04-2.11-848).

References

1. Jonker GH (1969) Philips Res Rep 24:1
2. Matsuura T, Tabuchi J, Mizusaki J, Yamauchi S, Fueki K (1988) J Phys Chem Solids 49(12):1403
3. Mizusaki J (1992) Solid State Ionics 52:79
4. Petrov AN, Kononchuk OF, Andreev AV, Cherepanov VA, Kofstad P (1995) Solid State Ionic 80:189
5. Kharton VV, Naomovich EN, Vecher AA, Nikolaev AV (1995) J Solid State Chem 120:128
6. Sehlin SR, Anderson HU, Sparlin DM (1995) Phys Rev B 52:11681
7. Raccah PM, Goodenenough JB (1967) Phys Rev 155:932
8. Kharton VV, Naumovich EN, Kovalevsky AV, Viskup AP, Figueiredo FM, Bashmakov A, Marques FMB (2000) Solid State Ionics 138:135
9. Petrov AN, Zuev AYu, Vylkov AI (2005) Russian J Phys Chem 79(2):220
10. Thornton G, Owen IW, Diakun GP (1991) J Phys Condens Matter 3:417
11. Senaris-Rodriguez MA, Goodenough JB (1995) J Solid State Chem 116:224
12. Kozhevnikov VL, Leonidov IA, Mitberg EB, Patrakeev MV, Petrov AN, Poeppelmeier KR (2003) J Solid State Chem 172:296
13. Doumerc J-P (1994) J Solid State Chem V.110:419
14. Goodenough JB (1970) Mater Res Bull V. 5:621
15. Zuev AYu, Petrov AN, Vylkov AI, Tsvetkov DS (2006) J Mater Sci. doi: 10.1007/s10853-006-0345-8
16. Heikes RR (1961) Thermoelectricity: science and engineering. Eds. by Heikes RR, Ure RW Interscience, New York, p 351