ISSN 0020-1685, Inorganic Materials, 2006, Vol. 42, No. 2, pp. 196–201. © Pleiades Publishing, Inc., 2006.
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Thermodynamic and Structural Properties of $PrBaCo_2O_{5+\delta}$

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Received April 21, 2005; in final form, August 25, 2005

Abstract—The oxygen content of the double cobaltite $PrBaCo_2O_{5+\delta}$ was determined by coulometric titration in broad temperature and oxygen pressure ranges, and the partial thermodynamic functions of oxygen were evaluated. The results on the nonstoichiometry and structural properties of $PrBaCo_2O_{5+\delta}$ demonstrate that, at $5 + \delta < 5.3$, this cobaltite has a high-temperature phase with lattice parameters $a = 11.774$ Å, $b = 11.932$ Å, and $c = 7.609$ Å. The composition dependences of $\Delta\bar{H}(O)$ and $\Delta\bar{S}(O)$ indicate that the $3a_p \times 3a_p \times 2a_p$ orthorhombic structure persists in the range $5.15 \le 5 + \delta \le 5.30$. Some of the Co^{3+} ions are shown to disproportionate according to the scheme $2Co^{3+} = Co^{2+} + Co^{4+}$.

DOI: 10.1134/S0020168506020154

INTRODUCTION

Partial substitution of alkaline-earth metals for rare-earth metals in $RCoO_3$ cobaltites leads to a number of effects associated primarily with the size factor and the mechanism underlying the charge compensation of acceptors. These effects include a tendency toward A-site ordering, changes in the oxidation state of the cobalt ions, and the development of significant oxygen nonstoichiometry. For example, substitution of barium for half of the rare-earth ions leads to the formation of $RBaCo_2O_{5+\delta}$ double perovskites in which δ may vary from 0 to 1 [1].

This broad range of oxygen stoichiometries in the double cobaltites is of considerable interest because it allows one to control the relative amounts of cobalt in different valence states. Moreover, a change from octahedral to pyramidal coordination influences the electronic configuration of the cobalt ions through changes in crystal-field parameters [2]. Given that Co^{3+} ions tend to disproportionate, resulting in high concentrations of Co^{2+} and Co^{4+} ions, which may be in several spin states, like Co^{3+}, the $RBaCo_2O_{5+\delta}$ oxides are convenient model systems for studying the properties of materials containing 3*d* cations in various electronic configurations. For this reason, double cobaltites are now receiving ever increasing attention.

Note that many questions regarding the nature of the ordered state in the double cobaltites still remain open. In this paper, we report our findings on the structural properties of $PrBaCo_2O_{5+\delta}$ and the effect of oxygen content on the thermodynamic properties of this cobaltite.

EXPERIMENTAL

$PrBaCo_2O_{5+\delta}$ was prepared by solid-state reaction. A stoichiometric mixture of Pr_6O_{11}, Co_3O_4, and $BaCO_3$ was reacted in air at temperatures from 900 to 1150°C with several intermediate grindings. After firing at 1150°C, the sample was slowly cooled to room temperature. To prepare samples with reduced oxygen contents, $PrBaCo_2O_{5+\delta}$ synthesized in air was then fired in a helium atmosphere ($p_{O_2} = 10^2$ Pa) at temperatures from 300 to 900°C for 2 h, followed by cooling to room temperature.

The phase composition of the resultant materials was determined by x-ray diffraction (XRD) analysis (Stoe Stadi-P diffractometer, CuK_{α_1} radiation, $\lambda = 1.54051$ Å, step size of 0.02°, $2\theta = 10°–100°$) at room temperature. The XRD data were analyzed using the Fullprof program [3].

The oxygen content of the samples was determined by thermogravimetry, using a SETARAM TG-92 thermoanalytical system. The samples were reduced by heating in a 5% H_2 + 95% He gas mixture to give BaO, Pr_2O_3, and cobalt metal. The associated weight loss was used to evaluate the oxygen content of the as-prepared sample.

The equilibrium oxygen content of the cobaltite as a function of temperature and oxygen partial pressure in the gas phase was determined by coulometric titration. Measurements were made isothermally in a stabilized zirconia electrochemical cell in the form of a tube to which a lid of the same material, with the platinum electrodes of the oxygen sensor and oxygen pump, was attached with high-temperature adhesive. The sample was placed in an alundum container, which was then mounted in the tube. The temperature was monitored with a Pt–30% Rh/Pt–6% Rh thermocouple. In electrical measurements, we used a Solartron 7081 precision voltmeter and a Solartron 1286 electrochemical interface as a controllable current source. The measuring cell was sealed in flowing oxygen at 1070°C and then cooled to 950°C. The oxygen content determined by thermogravimetry at 650°C and $p_{O_2} = 2.1 \times 10^4$ Pa was used as a reference point in coulometric titration experiments.

RESULTS AND DISCUSSION

Effect of oxygen content on structural parameters. $PrBaCo_2O_{5+\delta}$ synthesized in air had an orthorhombic structure (sp. gr. *Pmmm*) with lattice parameters a = 3.8981(1) Å, b = 7.7069(2) Å, and c = 7.6354(2) Å. The value of δ was 0.77. In the XRD patterns of the samples with other δ values, all of the reflections could be indexed in the same orthorhombic cell, $a_p \times 2a_p \times 2a_p$.

The lattice parameters, unit-cell volume V, and δ of our samples are listed in the table.

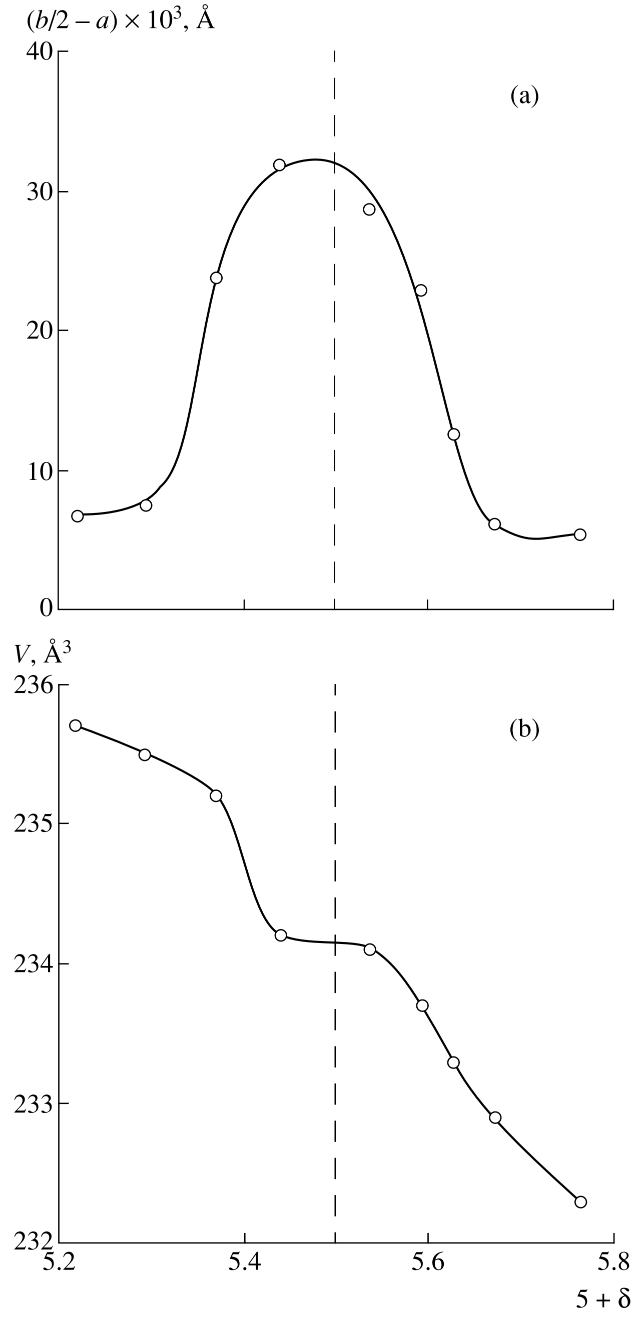

Fig. 1. Effect of oxygen content on the structural parameters of $PrBaCo_2O_{5+\delta}$.

Figure 1a shows the difference $b/2 - a$ as a function of oxygen content. The difference between a and $b/2$ has a maximum near the composition $PrBaCo_2O_{5.5}$, where the average charge state of the cobalt ions is 3+. The maximum in $b/2 - a$ as a function of 5 + δ points to ordering of oxygen vacancies along the a axis. Moreover, it seems likely that, just as in $TbBaCo_2O_{5.5}$ [2], a structural analog of $PrBaCo_2O_{5.5}$, this difference is partially due to the strong difference between the a- and b-axis Co–O bond lengths in the $Co^{3+}O_5$ pyramids and $Co^{3+}O_6$ octahedra, associated with $(d_{3x^2-r^2}/d_{3y^2-r^2})$ orbital ordering. The decrease in unit-cell volume at 5 + δ > 5.5 (Fig. 1b) is mainly due to the drop in b, which is caused by the distortion of the $Co^{3+}O_6$ octahedra at increased oxidation states of the cobalt ions. The rise in unit-cell volume for 5 + δ < 5.5 is related primarily to the increase in a with decreasing δ, which is associated both with the change from $Co^{3+}O_6$ octahedra (elongated along the b axis) to $Co^{3+}O_5$ pyramids (elongated along the a axis) and the partial reduction of cobalt, leading to the formation of the larger sized ions Co^{2+} in $Co^{2+}O_5$ pyramids.

Effect of temperature and oxygen pressure on the oxygen content and structure. Figure 2 shows the equilibrium oxygen content of $PrBaCo_2O_{5+\delta}$ as a function of oxygen partial pressure in the temperature range 650–950°C. Under these conditions, 5 + δ varies from 5.0 to 5.56. The kinks near δ = 1/3 in the range 750–850°C suggest the formation of a high-temperature

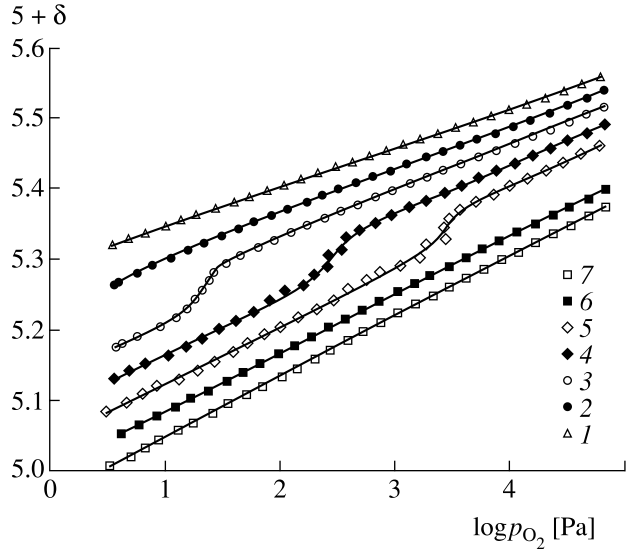

Fig. 2. Oxygen content of $PrBaCo_2O_{5+\delta}$ as a function of oxygen partial pressure in the gas phase at (*1*) 650, (*2*) 700, (*3*) 750, (*4*) 800, (*5*) 850, (*6*) 900, and (*7*) 950°C.

phase of $PrBaCo_2O_{5+\delta}$, which has not been described previously.

To confirm this assumption, the cobaltite was fired at 1000°C in an He atmosphere ($p_{O_2} = 10^2$ Pa) and then quenched in liquid gallium. As would be expected, the XRD pattern of that sample showed that the high- and low-temperature phases of $PrBaCo_2O_{5+\delta}$ differed significantly in structural parameters (Fig. 3). The oxygen ordering near $\delta = 1/3$ give grounds to expect that the lattice parameters of the high-temperature phase are related by $a \approx b \approx 3a_p$. Indeed, all of the reflections in the XRD pattern of the high-temperature phase can be indexed in a $3a_p \times 3a_p \times 2a_p$ orthorhombic cell with a = 11.774 Å, b = 11.932 Å, and c = 7.609 Å. The large difference $b/3 - a/3 = 0.052$ Å indicates that the CoO_5 pyramids in the high-temperature phase are elongated along the b axis, just as in $PrBaCo_2O_{5.5}$. It should be emphasized that $PrBaCo_2O_{5+\delta}$ with a $3a_p \times 3a_p \times 2a_p$ cell is formed at $\delta < 0.33$ and temperatures above 700°C (Fig. 2) and can be quenched to room temperature. According to XRD results (table), $PrBaCo_2O_{5+\delta}$ samples with $0.22 < \delta < 0.77$ slowly cooled to room temperature have an $a_p \times 2a_p \times 2a_p$ cell.

Oxygen content and lattice parameters of $PrBaCo_2O_{5+\delta}$

$5 + \delta$	a, Å	b, Å	c, Å	V, Å^3
5.765	3.8981	7.8069	7.6345	232.3
5.673	3.9036	7.8195	7.6291	232.9
5.629	3.9040	7.8332	7.6296	233.3
5.595	3.9038	7.8534	7.6214	233.7
5.538	3.9058	7.8690	7.6157	234.1
5.441	3.9075	7.8786	7.6068	234.2
5.371	3.9177	7.8830	7.6171	235.2
5.294	3.9304	7.8758	7.6074	235.5
5.22	3.9342	7.8818	7.5999	235.7

Thermodynamic properties of weakly bound oxygen. The data presented in Fig. 2 can be used to evaluate the chemical potential of weakly bound oxygen, $\Delta\mu_O$, in $PrBaCo_2O_{5+\delta}$ relative to the standard state in the gas phase since, in thermodynamic equilibrium, the difference in the chemical potential of oxygen between the gas phase and the cobaltite is constant:

$$\begin{aligned} \Delta\mu_O \equiv \mu_O(PrBaCo_2O_{5+\delta}) - 1/2\mu^0_{O_2} \\ = 1/2RT\ln p_{O_2}. \end{aligned} \quad (1)$$

The results indicate that, in both polymorphs, the chemical potential is a linear function of temperature at fixed δ. In view of this, we determined the partial molar enthalpy $\Delta\bar{H}$(O) and entropy $\Delta\bar{S}$(O) of oxygen by the standard formula

$$\Delta\mu_O = \Delta\bar{H}(O) - T\Delta\bar{S}(O). \quad (2)$$

The results are presented in Fig. 4. At $5 + \delta < 5.33$, the enthalpy is a weak function of the oxygen content of the high-temperature phase with the $3a_p \times 3a_p \times 2a_p$ cell. In contrast, the entropy varies rapidly in this composition range, which is associated with the reduction in the concentration of vacancies accessible to oxygen. The complex shape of the $\Delta\bar{H}$(O) and $\Delta\bar{S}$(O) curves at $5 + \delta > 5.33$ indicates that oxygen is incorporated in at least two types of vacant sites, differing in energy. The increase in $\Delta\bar{H}$(O) and $\Delta\bar{S}$(O) with δ at $5 + \delta > 5.33$ indicates that oxygen begins to occupy energetically less favorable sites. One possible reason for this behavior of $\Delta\bar{H}$(O) and $\Delta\bar{S}$(O) is that, as the oxygen stoichiometry approaches $5 + \delta = 5.5$, some of the oxygen ions undergo local ordering, as, e.g., in the low-temperature orthorhombic cell $a_p \times 2a_p \times 2a_p$ of $PrBaCo_2O_{5.5}$.

The incorporation of oxygen into vacancies V_O in $PrBaCo^{2+}Co^{3+}O_{5+\delta}$ can be represented by the reaction scheme

$$1/2O_2 + V_O + 2Co^{2+} = O^{2-} + 2Co^{3+}. \quad (3)$$

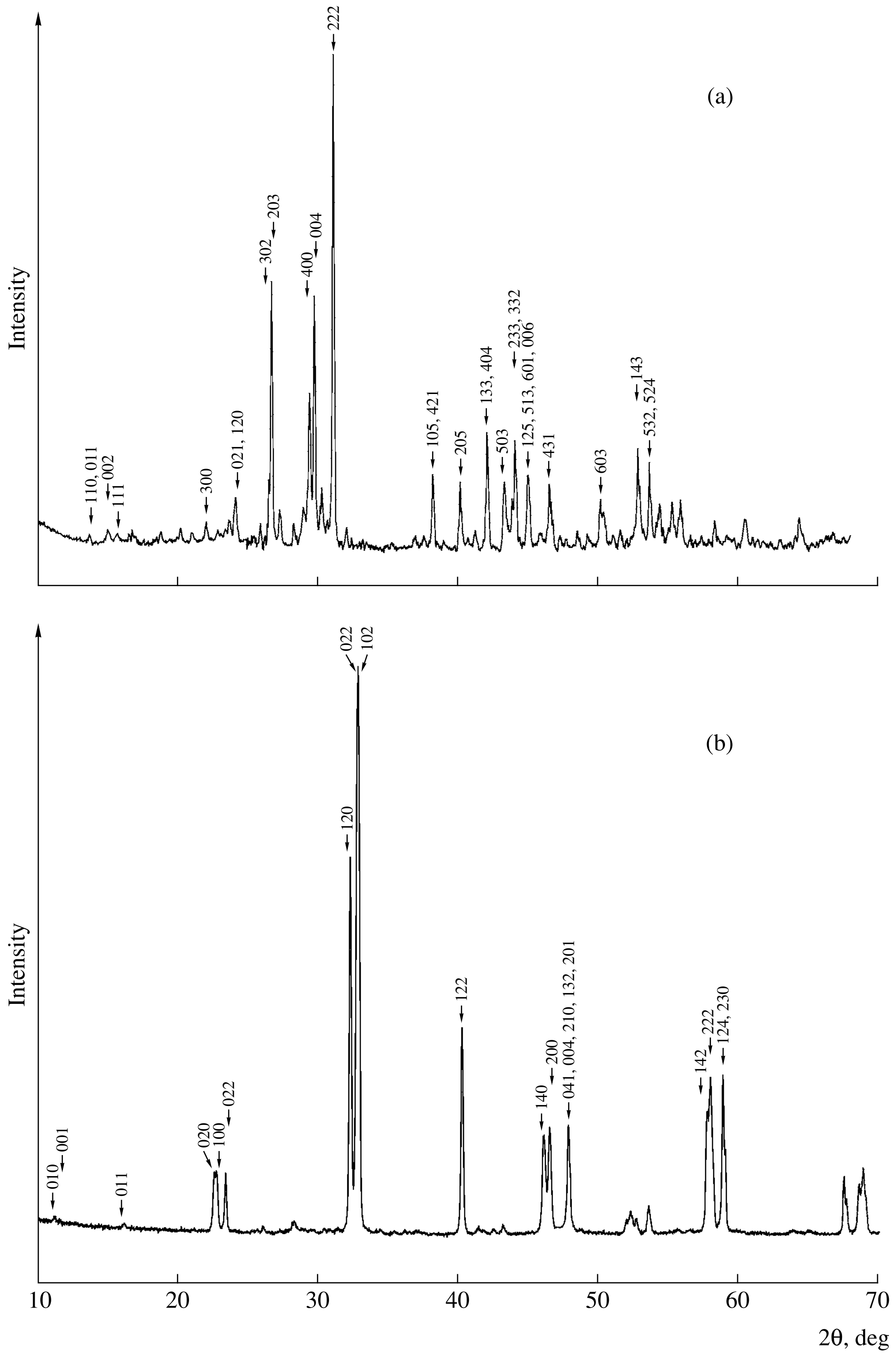

Fig. 3. XRD patterns of $PrBaCo_2O_{5+\delta}$ samples fired in a helium atmosphere ($p_{O_2} = 10^2$ Pa) and then (a) quenched from 1000°C or (b) cooled from 600°C.

The equilibrium constant of reaction (3),

$$K_p = \frac{[O^{2-}][Co^{3+}]^2}{[V_O][Co^{2+}]^2} pO_2^{-1/2}, \qquad (4)$$

can be expressed through the standard enthalpy and entropy:

$$-RT\ln K_p = \Delta_r H^0 - T\Delta_r S^0. \qquad (5)$$

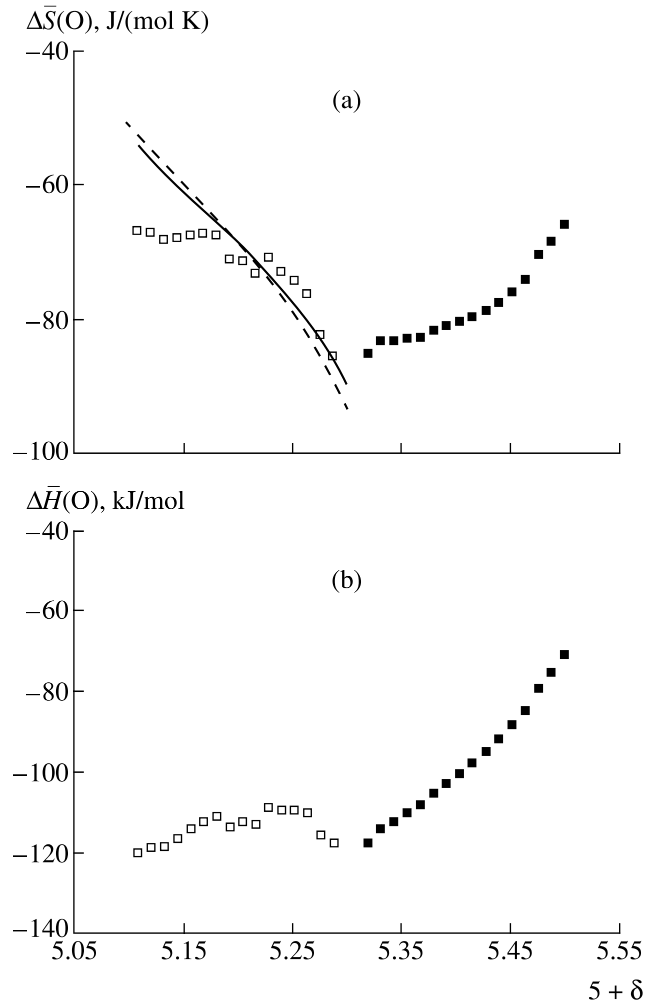

Fig. 4. Partial molar (a) entropy and (b) enthalpy as functions of oxygen content; the dashed and solid lines represent calculations by Eqs. (8) and (10), respectively.

Combining (1), (2), (4), and (5), we obtain

$$\Delta\bar{H}(\mathrm{O}) - T\Delta\bar{S}(\mathrm{O}) = \Delta_r H^0 - T\left(\Delta_r S^0 + R\ln\frac{[V_\mathrm{O}][\mathrm{Co}^{2+}]^2}{[\mathrm{O}^{2-}][\mathrm{Co}^{3+}]^2}\right). \qquad (6)$$

Therefore,

$$\Delta\bar{H}(\mathrm{O}) = \Delta_r H^0$$

and

$$\Delta\bar{S}(\mathrm{O}) = R\ln\frac{[V_\mathrm{O}][\mathrm{Co}^{2+}]^2}{[\mathrm{O}^{2-}][\mathrm{Co}^{3+}]^2} + \Delta_r S^0. \qquad (7)$$

For $5 + \delta < 5.5$, the composition of the cobaltite can be written in the form $\mathrm{PrBaCo}^{2+}_{1-2\delta}\mathrm{Co}^{3+}_{1+2\delta}\mathrm{O}_{5+\delta}$. Under the assumption that the concentration of vacancies accessible to oxygen in the high-temperature phase is close to $[V_\mathrm{O}] = 0.33 - \delta$, Eq. (7) for entropy takes the form

$$\Delta\bar{S}(\mathrm{O}) = R\ln\frac{(0.33-\delta)(1-2\delta)^2}{\delta(1+2\delta)^2} + \Delta_r S^0. \qquad (8)$$

As seen in Fig. 4, the partial molar entropy of oxygen in $\mathrm{PrBaCo_2O_{5+\delta}}$ calculated by Eq. (8) with $\Delta_r S^0 = -51$ J/(mol K) agrees with experimental data only in the narrow composition range $0.17 < \delta < 0.25$. The discrepancy between the calculation results and experimental $\Delta\bar{S}$(O) data can be reduced by taking into account that some of the Co^{3+} ions (2α) disproportionate according to the reaction

$$2\mathrm{Co}^{3+} = \mathrm{Co}^{2+} + \mathrm{Co}^{4+}. \qquad (9)$$

With allowance made for this process, the crystal-chemical formula of the cobaltite can be represented as $\mathrm{PrBaCo}^{2+}_{1-2\delta+\alpha}\mathrm{Co}^{3+}_{1+2\delta-2\alpha}\mathrm{Co}^{4+}_{\alpha}\mathrm{O}_{5+\delta}$.

Note that Co^{3+} disproportionation accounts for the high hole conductivity of $\mathrm{PrBaCo_2O_{5+\delta}}$, which is 100 S/cm at $\delta = 0$ and 400 S/cm at $\delta = 0.5$ (Fig. 5). Moreover, since conductivity is proportional to the product of the Co^{3+} and Co^{4+} concentrations [4], the increase in this product by a factor of 4 as δ increases from 0 to 0.5 indicates that the disproportionation parameter is a function of composition. Clearly, for $\delta \longrightarrow 0$ this function approaches some constant. Given this, one can show by simple calculations that the relation $\alpha = 0.15 + \delta^2$ provides a good fit to the conductivity versus oxygen content data. The partial entropy of the cobaltite can then be expressed in the form

$$\Delta\bar{S}(\mathrm{O}) = R\ln\frac{(0.33-\delta)(1-2\delta+\alpha)^2}{\delta(1+2\delta-2\alpha)^2} + \Delta_r S^0. \qquad (10)$$

Figure 4 demonstrates that Eq. (10) with $\Delta_r S^0 = -62$ J/(mol K) gives a good fit to the experimental ΔS(O) data over most of the composition range of the high-temperature phase of $\mathrm{PrBaCo_2O_{5+\delta}}$ with the $3a_\mathrm{p} \times 3a_\mathrm{p} \times 2a_\mathrm{p}$ cell. The discrepancy between the experimental $\Delta\bar{S}$(O) data and calculation results at $\delta < 0.15$ is attributable to the possible formation of small $\mathrm{PrBaCo_2O_5}$-type $a_\mathrm{p} \times a_\mathrm{p} \times 2a_\mathrm{p}$ domains (clusters) as δ approaches zero. The number of vacancies accessible to oxygen in such domains is obviously smaller than that in the $3a_\mathrm{p} \times 3a_\mathrm{p} \times 2a_\mathrm{p}$ cell. For $5 + \delta > 5$, such vacancies are rapidly filled with oxygen and, according to Eq. (7), the entropy decreases.

In the study by Maignan *et al.* [1], the formation of a domain structure in $\mathrm{LnBaCo_2O_{5+\delta}}$ nonstoichiometric cobaltites with different subcell dimensions was revealed by electron diffraction and high-resolution microscopy. $\mathrm{HoBaCo_2O_{5.3}}$ was shown to consist of

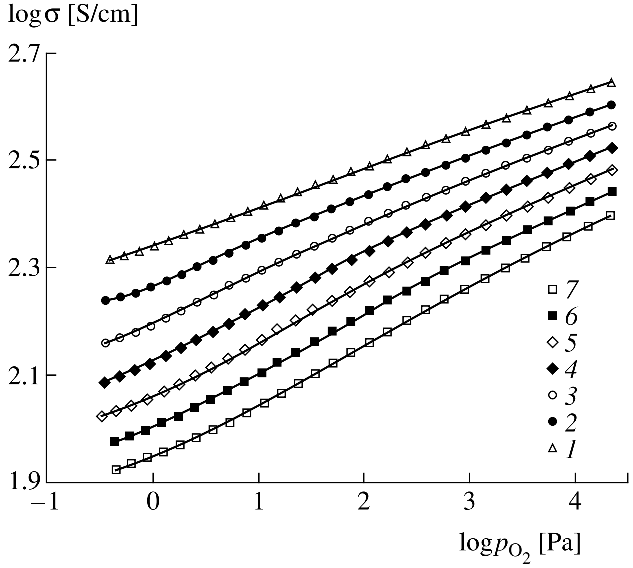

Fig. 5. Log–log plots of hole conductivity vs. oxygen partial pressure in the gas phase for $PrBaCo_2O_{5+\delta}$ at (*1*) 650, (*2*) 700, (*3*) 750, (*4*) 800, (*5*) 850, (*6*) 900, and (*7*) 950°C.

$3a_p \times 3a_p \times 2a_p$ domains. At the same time, the XRD pattern of this cobaltite can be indexed with high accuracy in a homogeneous orthorhombic structure with an $a_p \times 2a_p \times 2a_p$ cell.

CONCLUSIONS

The present results on the nonstoichiometry and structural properties of $PrBaCo_2O_{5+\delta}$ demonstrate that, at $5 + \delta < 5.3$, this cobaltite has a high-temperature phase with lattice parameters $a = 11.774$ Å, $b = 11.932$ Å, and $c = 7.609$ Å.

Thermodynamic analysis indicates that the $3a_p \times 3a_p \times 2a_p$ long-range order persists in the range $5.15 \le 5 + \delta \le 5.30$. These stability limits of the high-temperature phase are close to $\delta = 1/9$ and $1/3$, corresponding, respectively, to one and three occupied oxygen sites in the *ab* plane of the $3a_p \times 3a_p \times 2a_p$ cell. For $\delta < 0.11$ and $\delta > 0.33$, this cobaltite seems to contain domains with another structure, $PrBaCo_2O_5$ and $PrBaCo_2O_{5.5}$, respectively, even at high temperatures.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 04-03-32948.

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