

## Research Article

# Oxygen Content and Thermodynamic Stability of $\text{YBaCo}_2\text{O}_{6-\delta}$ Double Perovskite

Anton L. Sednev, Andrey Yu Zuev, and Dmitry S. Tsvetkov 

*Institute of Natural Sciences and Mathematics, Ural Federal University, Yekaterinburg 620000, Russia*

Correspondence should be addressed to Dmitry S. Tsvetkov; [dmitry.tsvetkov@urfu.ru](mailto:dmitry.tsvetkov@urfu.ru)

Received 7 September 2017; Revised 20 October 2017; Accepted 10 December 2017; Published 13 February 2018

Academic Editor: Pascal Roussel

Copyright © 2018 Anton L. Sednev et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The thermodynamic stability of the double perovskite  $\text{YBaCo}_2\text{O}_{6-\delta}$  was studied using the coulometric titration technique and verified by measurements of the overall conductivity depending on oxygen partial pressure at a given temperature. As a result, the stability diagram of  $\text{YBaCo}_2\text{O}_{6-\delta}$  was plotted.  $\text{YBaCo}_2\text{O}_{6-\delta}$  was found to be thermodynamically stable in air at 850°C and higher temperatures, whereas its thermodynamic stability at 900°C is limited by the range of oxygen partial pressures  $-3.56 \leq \log(p\text{O}_2/\text{atm}) \leq -0.14$ . Oxygen content in  $\text{YBaCo}_2\text{O}_{6-\delta}$  slightly decreases at 900°C from 5.035 at  $\log(p\text{O}_2/\text{atm}) = -0.14$  to 4.989 in the atmosphere with  $\log(p\text{O}_2/\text{atm}) = -3.565$  indicating a crucial role which variation of  $\text{Co}^{+3}/\text{Co}^{+2}$  ratio plays in its stability.  $\text{YBaCo}_2\text{O}_{6-\delta}$  decomposes into the mixture of  $\text{YCoO}_3$  and  $\text{BaCoO}_{3-z}$  at the high  $p\text{O}_2$  stability limit, whereas  $\text{YBaCo}_4\text{O}_7$ ,  $\text{BaCo}_{1-x}\text{Y}_x\text{O}_{3-y}$ , and  $\text{Y}_2\text{O}_3$  were identified as the products of its decomposition at the low  $p\text{O}_2$  one.

## 1. Introduction

Cobaltites  $\text{REBaCo}_2\text{O}_{6-\delta}$ , where RE is a rare earth metal, with the double perovskite structure have attracted great attention in the past decade due to their unique properties such as high oxide ion and electronic conductivity as well as very promising activity as cathodes in IT SOFCs [1–5]. Despite the fascinating properties of these materials, their successful commercial application as cathodes is restricted by large thermal expansion coefficient (CTE), which significantly exceeds CTE of the state-of-the-art electrolyte materials [4]. Nevertheless, there is a trend of lowering CTE with decreasing size of RE [4]. In this respect,  $\text{YBaCo}_2\text{O}_{6-\delta}$  has advantage as compared to other double perovskites since it has the lowest CTE among all  $\text{REBaCo}_2\text{O}_{6-\delta}$  oxides, which is close to that of doped ceria and zirconia, the state-of-the-art SOFC electrolytes [1–6]. This double perovskite was found to have the total conductivity high enough for using it as a cathode for IT SOFCs [6–15]. As a result, materials on the basis of  $\text{YBaCo}_2\text{O}_{6-\delta}$  showed high performance as cathodes of IT SOFCs [6, 9, 10, 12, 15] and oxygen permeable membranes [16, 17]. It is generally recognized that knowledge of the thermodynamic stability limits of oxides materials is of key importance for understanding their properties and, therefore,

their successful application in electrochemical devices for energy conversion and storage. However, the thermodynamic stability of  $\text{YBaCo}_2\text{O}_{6-\delta}$  is poorly understood, and it remains a controversial topic so far. The authors [14, 15] by means of X-ray diffraction (XRD) found secondary phases in samples of  $\text{YBaCo}_2\text{O}_{6-\delta}$  annealed at temperatures between 800°C and 850°C depending on ambient atmosphere and concluded that this oxide is unstable under aforementioned conditions. It is worth noting that, according to Kim et al. [15],  $\text{YBaCo}_2\text{O}_{6-\delta}$  is unstable at 800°C in air while it was found [14] that this oxide is quite stable in air even at 850°C. On the contrary,  $\text{YBaCo}_2\text{O}_{6-\delta}$  was found to be unstable at 850°C in atmosphere of nitrogen [14], whereas there is no evidence of this oxide decomposition at 800°C in the same ambient atmosphere [15]. Moreover, if  $\text{YBaCo}_2\text{O}_{6-\delta}$  is unstable at certain temperature, then one could expect a singularity of temperature dependences of its oxygen content, electrical conductivity, and CTE at this temperature. However, there is no evidence of such singularity in literature except the work of Xue et al. [6] where the authors observed something like that for CTE of  $\text{YBaCo}_2\text{O}_{6-\delta}$  at 800°C and 850°C. However, Xue et al. [6] did not comment this singularity, which was not confirmed in other works.

Thus, the priority purpose of the present work was to obtain reliable data on the thermodynamic stability of  $\text{YBaCo}_2\text{O}_{6-\delta}$  by means of three independent methods such as coulometric titration, conductivity measurements, and homogenizing annealing of samples in atmosphere with controlled oxygen partial pressure. The novelty of the work consists in the constructing of the thermodynamic stability diagram for interesting and promising double perovskite  $\text{YBaCo}_2\text{O}_{6-\delta}$  for the first time.

## 2. Materials and Methods

The powder samples of single phase  $\text{YCoO}_3$ ,  $\text{BaCo}_2\text{O}_3$ , and  $\text{YBaCo}_2\text{O}_{6-\delta}$  were synthesized by means of glycerol-nitrate technique using  $\text{Co}$ ,  $\text{Y}_2\text{O}_3$ , and  $\text{BaCO}_3$  as starting materials.  $\text{Y}_2\text{O}_3$  and  $\text{BaCO}_3$  had a purity of 99.99%. Metallic  $\text{Co}$  was obtained by reduction of  $\text{Co}_3\text{O}_4$  (purity 99.99%) in  $\text{H}_2$  atmosphere at  $600^\circ\text{C}$ .  $\text{Y}_2\text{O}_3$  and  $\text{BaCO}_3$  were preliminary calcined in air at  $1100^\circ\text{C}$  and  $600^\circ\text{C}$ , respectively, for removal of adsorbed  $\text{H}_2\text{O}$  and  $\text{CO}_2$ .

Stoichiometric mixture of starting materials was dissolved in concentrated nitric acid (99.99% purity), and required volume of glycerol (99% purity) was added as a complexing agent and a fuel. Glycerol quantity was calculated according to full reduction of corresponding nitrates to molecular nitrogen  $\text{N}_2$ . The as-prepared solutions were heated continuously at  $100^\circ\text{C}$  until complete water evaporation and pyrolysis of the dried precursor had occurred. The resulting ash was subsequently calcined for 10 hours at  $1100^\circ\text{C}$  for  $\text{BaCo}_2\text{O}_3$  as well as  $\text{YBaCo}_2\text{O}_{6-\delta}$  and  $900^\circ\text{C}$  for  $\text{YCoO}_3$  to get the desired oxide powder.

The phase composition of the powder samples prepared accordingly was studied at room temperature by means of X-ray diffraction (XRD) with XRD-7000 diffractometer (Shimadzu, Japan) using  $\text{Cu K}\alpha$  radiation. XRD showed no indication of the presence of a second phase for the as-prepared oxides.

The chemical composition of all the oxides prepared was checked using an ICP spectrometer ICAP 6500 DUO and an atomic absorption spectrometer Solaar M6 (both supplied by Thermo Scientific, USA). All the as-prepared oxides were shown to have the stoichiometric composition with respect to metal cations within the accuracy of 2%. No impurities were found within the same accuracy range as well.

For the measurements of electrical conductivity, single phase powder of  $\text{YBaCo}_2\text{O}_{6-\delta}$  was axially pressed into rectangular bars of  $30 \times 4 \times 4 \text{ mm}^3$  at 40 MPa and sintered at  $1150^\circ\text{C}$  for 24 h in air. The relative density of the sample bars used for measurements was found to be higher than 80%.

Thermodynamic stability limits of  $\text{YBaCo}_2\text{O}_{6-\delta}$  were determined by three independent methods such as coulometric titration combined with EMF method, electrical conductivity measurements, and homogenizing annealing of samples in atmosphere with controlled oxygen partial pressure. The coulometric titration was also employed for measurements of the oxygen nonstoichiometry in  $\text{YBaCo}_2\text{O}_{6-\delta}$  as a function of  $p\text{O}_2$  at a given temperature. The original coulometric titration setup and the measurement procedure are described in detail elsewhere [18, 19].

Total conductivity of  $\text{YBaCo}_2\text{O}_{6-\delta}$  oxide as a function of  $p\text{O}_2$  at a given temperature was measured using 4-probe dc-method, and the original setup described in detail elsewhere [20].

Absolute value of  $\delta$  in  $\text{YBaCo}_2\text{O}_{6-\delta}$  sample was determined by direct reduction by hydrogen flux in the TG setup (TG/H<sub>2</sub>). Experimental details for this method are given elsewhere [19].

For homogenizing annealing experiments, samples of two different compositions were employed. The first one was equimolar mixture of  $\text{YCoO}_3$  and  $\text{BaCo}_2\text{O}_3$ , whereas the second one was single phase powder of  $\text{YBaCo}_2\text{O}_{6-\delta}$ . In both cases, a sample was heated first to  $700^\circ\text{C}$  in an atmosphere with a given  $p\text{O}_2$  and then was equilibrated at this temperature for 72 h followed by quenching to room temperature. After that, the quenched sample was grinded in mortar, and its phase composition was determined by XRD. Then, annealing temperature was increased on  $100^\circ\text{C}$ , and the rest of the experimental procedure was similar to that described above. After annealing at the highest temperature, the gas atmosphere surrounding the sample was changed, and measurement procedure was repeated as described above. Oxygen partial pressure in the gas atmosphere around the sample was adjusted using a YSZ-based electrochemical oxygen pump installed in the outer regulating unit and governed by the automatic controller (Zirconia 318, Russia). Three gas atmospheres with  $p\text{O}_2 = 1, 0.21, \text{ and } 10^{-3}$  adjusted accordingly with gas flow rate of about 50 ml/min (to avoid oxygen partial pressure gradients along the sample) were used.

## 3. Results and Discussion

**3.1. Sample Characterization.** X-ray diffraction patterns of the as-prepared single phase powder samples of  $\text{YCoO}_3$ ,  $\text{YBaCo}_2\text{O}_{6-\delta}$ , and  $\text{BaCo}_2\text{O}_3$  are given in Figures 1–3, respectively. It should be mentioned that the pattern of  $\text{BaCo}_2\text{O}_3$  was interpreted as a mixture of two compounds  $\text{BaCo}_2\text{O}_3$  and  $\text{BaCo}_2\text{O}_{2.61}$ .

The space groups used for the XRD patterns indexing along with the refined cell parameters are given in Table 1 in comparison with those reported in literature.

As seen, the cell parameters found in the present study and those reported earlier are in good agreement with each other.

**3.2. Oxygen Nonstoichiometry and Thermodynamic Stability of  $\text{YBaCo}_2\text{O}_{6-\delta}$ .** Oxygen nonstoichiometry in  $\text{YBaCo}_2\text{O}_{6-\delta}$  as a function of  $T$  and  $p\text{O}_2$  was measured by means of coulometric titration technique in the ranges  $800 \leq (T, ^\circ\text{C}) \leq 1050$  and  $-5 \leq \log(p\text{O}_2/\text{atm}) \leq 0$ , respectively. Taking into account the absolute oxygen content determined by TG/H<sub>2</sub> ( $5.016 \pm 0.002$  at  $900^\circ\text{C}$  in air), the coulometric titration curves measured for  $\text{YBaCo}_2\text{O}_{6-\delta}$  at different temperatures were recalculated in  $p\text{O}_2$  dependences of its oxygen content,  $6-\delta$ , given in Figure 4.

As an example, such dependence obtained accordingly at  $900^\circ\text{C}$  is shown in Figure 5.

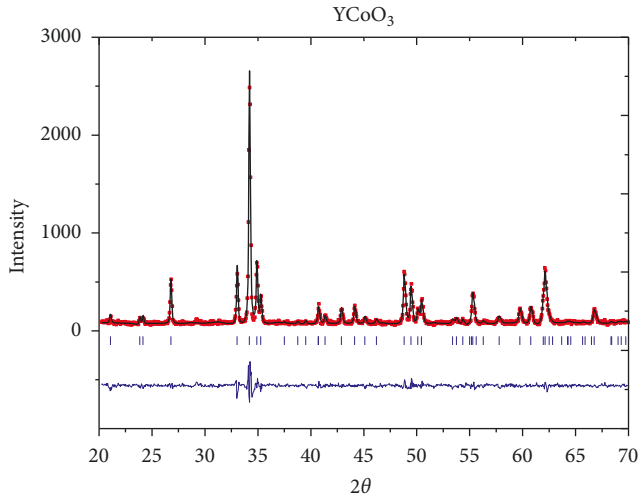
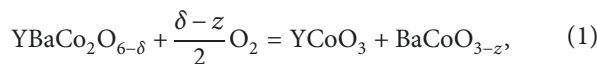


FIGURE 1: X-ray diffraction pattern and its matching refinement plot of  $\text{YCoO}_3$ : observed X-ray diffraction intensity (points) and calculated curve (line). The bottom curve is the difference of patterns,  $y_{\text{obs}} - y_{\text{cal}}$ , and the small bars indicate the angular positions of the allowed Bragg reflections.

Vertical segments of the titration curve (Figure 5) correspond to the sample decomposition and clearly indicate its thermodynamic stability limits with respect to reduction (at low  $p\text{O}_2$ ) and oxidation (at high  $p\text{O}_2$ ). The curve plot enclosed between vertical segments corresponds to the oxygen content change in  $\text{YBaCo}_2\text{O}_{6-\delta}$  within the thermodynamic stability region. It is worth noting that the  $p\text{O}_2$  dependence of oxygen content measured at this temperature and shown in Figure 5 exhibits inflection when oxygen content of the double perovskite reaches the value of 5. The same behavior was found earlier [18] for another double perovskite  $\text{GdBaCo}_2\text{O}_{6-\delta}$ . However, unlike  $\text{GdBaCo}_2\text{O}_{6-\delta}$  the double perovskite with yttrium possesses really narrow homogeneity range with respect to oxygen since oxygen content changes in the vicinity of 5 and its overall variation is less than 0.83% within the thermodynamic stability region at  $900^\circ\text{C}$ . In other words, such narrow homogeneity region corresponds to a small change of the average oxidation state of cobalt; that is, even slight reduction of  $\text{Co}^{3+}$  or oxidation of  $\text{Co}^{2+}$  may result in  $\text{YBaCo}_2\text{O}_{6-\delta}$  oxide decomposition. Coulometric measurements carried out at  $900^\circ\text{C}$  were stopped after reaching the highest  $p\text{O}_2$  value, 0.72 atm, and the coulometric cell was fast cooled down to room temperature. XRD of the  $\text{YBaCo}_2\text{O}_{6-\delta}$  sample cooled accordingly showed the presence of the yttrium cobaltite  $\text{YCoO}_3$  and the barium cobaltites  $\text{BaCoO}_3$  and  $\text{BaCoO}_{2.63}$  as products of  $\text{YBaCo}_2\text{O}_{6-\delta}$  decomposition. Taking into account possible oxygen nonstoichiometry of the complex oxides, a decomposition reaction can be written as



where a value of the oxygen content,  $6-\delta$ , depends on temperature and varies from 5.012 at  $800^\circ\text{C}$  up to 5.035 at  $900^\circ\text{C}$ . It is worth noting that reaction (1) is completely in line with the finding of the authors [15] that the perovskites

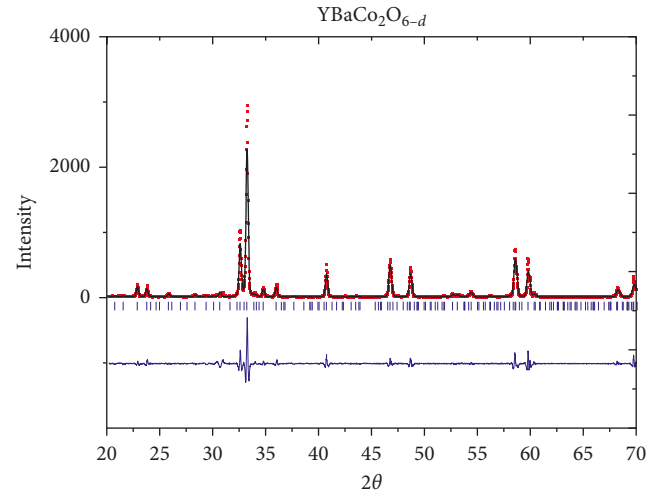


FIGURE 2: X-ray diffraction pattern and its matching refinement plot of  $\text{YBaCo}_2\text{O}_{6-\delta}$ : observed X-ray diffraction intensity (points) and calculated curve (line). The bottom curve is the difference of patterns,  $y_{\text{obs}} - y_{\text{cal}}$ , and the small bars indicate the angular positions of the allowed Bragg reflections.

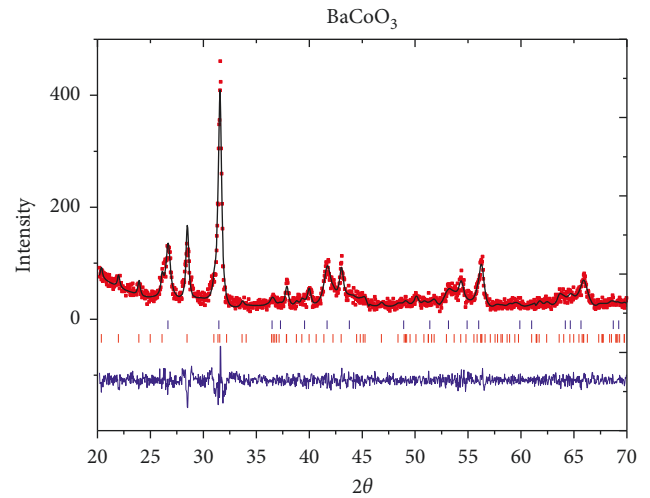


FIGURE 3: X-ray diffraction pattern and its matching refinement plot of  $\text{BaCoO}_3$ , interpreted as a mixture of  $\text{BaCoO}_3$  and  $\text{BaCoO}_{2.61}$ : observed X-ray diffraction intensity (points) and calculated curve (line). The bottom curve is the difference of patterns,  $y_{\text{obs}} - y_{\text{cal}}$ , and the small bars indicate the angular positions of the allowed Bragg reflections.

$\text{YCoO}_3$  and  $\text{BaCoO}_3$  are products of  $\text{YBaCo}_2\text{O}_{6-\delta}$  decomposition in air ( $p\text{O}_2 = 0.21$  atm) at temperatures lower than  $850^\circ\text{C}$ .

In order to find products of  $\text{YBaCo}_2\text{O}_{6-\delta}$  decomposition at low  $p\text{O}_2$  stability limit, its single phase sample was annealed at  $1000^\circ\text{C}$  in gas atmosphere with  $\log(p\text{O}_2/\text{atm}) = -4$  for 12 hours and then quenched to ice at  $-18^\circ\text{C}$ . The XRD pattern of the sample prepared accordingly showed the presence of  $\text{YBaCo}_4\text{O}_7$ ,  $\text{BaCo}_{1-x}\text{Y}_x\text{O}_{3-2z}$ , and  $\text{Y}_2\text{O}_3$ . Therefore, the decomposition of  $\text{YBaCo}_2\text{O}_{6-\delta}$  at low  $p\text{O}_2$  stability limit occurs according to the following reaction:

TABLE 1: Refined cell parameters and space groups of the as-prepared oxide compounds.

Compound	Space group	$a^*$ , Å	$b^*$ , Å	$c^*$ , Å	Reference
YBaCo <sub>2</sub> O <sub>6-δ</sub>	P4/mmm	11.611	11.611	7.485	Present work
		11.616	11.616	7.493	[15]
		11.615	11.615	7.496	[8]
		11.616	11.616	7.497	[10]
YCoO <sub>3</sub>	Pbnm	5.139	5.419	7.365	Present work
		5.137	5.420	7.364	[21]
		5.132	5.411	7.360	[22]
BaCoO <sub>3</sub>	P-6m2	5.683	5.683	4.552	Present work
		5.645	5.645	4.752	[23]
		5.652	5.6525	4.763	[24]
BaCoO <sub>2.63</sub>	P63/mmc	5.666	5.666	28.494	Present work
		5.665	5.665	28.493	[25]
		5.671	5.671	28.545	[26]

\*Uncertainty  $\pm 0.001$  Å.

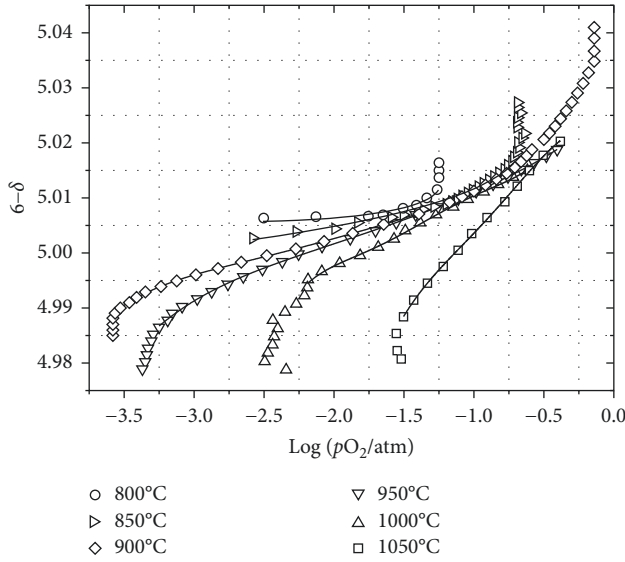
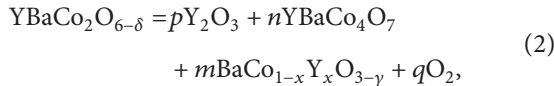


FIGURE 4: Oxygen content,  $6-\delta$ , in YBaCo<sub>2</sub>O<sub>6-δ</sub> versus  $pO_2$  at different temperatures. Points correspond to experimental data and lines are guide to eye only.



where  $m = 2/(3+x)$ ,  $n = (1+x)/(3+x)$ ,  $p = -(1/2)((3x+1)/(3+x))$ , and  $q = -(1/4)((-13+6\delta-4\gamma-7x+2x\delta)/(3+x))$ , since the oxygen content in the hexagonal YBaCo<sub>4</sub>O<sub>7</sub> is very close to 7 in the vicinity of its low  $pO_2$  stability limit; for example, it comes to 6.99 at 900°C and  $\log(pO_2/atm) = -3.5$  [27].

It is worth noting that decomposition of YBaCo<sub>2</sub>O<sub>6-δ</sub> is quite different from that of another double perovskite, for instance GdBaCo<sub>2</sub>O<sub>6-δ</sub>, which decomposes at low  $pO_2$  according to completely different reaction [28]:

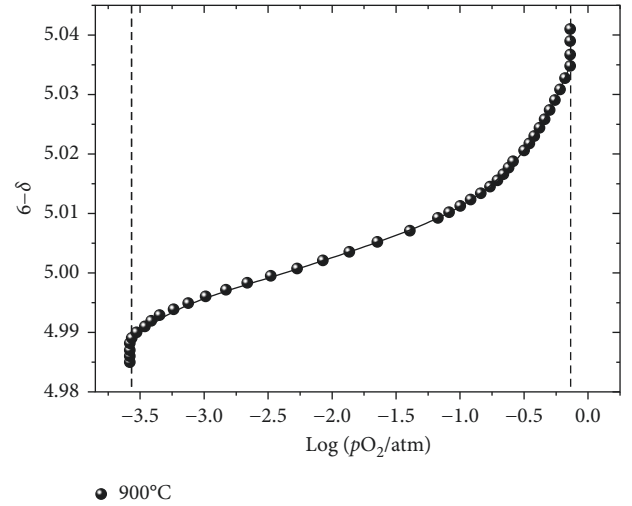
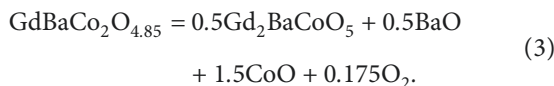


FIGURE 5: Oxygen content,  $6-\delta$ , in YBaCo<sub>2</sub>O<sub>6-δ</sub> versus  $pO_2$  at 900°C. Points correspond to experimental data and line is guide to eye only.

Thermodynamic stability limits of YBaCo<sub>2</sub>O<sub>6-δ</sub> determined accordingly are summarized in the stability diagram shown in Figure 6 as  $\log(pO_2) = f(1/T)$ .

A nonlinear character of  $\log(pO_2) = f(1/T)$  dependence corresponding to low  $pO_2$  stability limit of YBaCo<sub>2</sub>O<sub>6-δ</sub> is related probably to a real composition of BaCo<sub>1-x</sub>Y<sub>x</sub>O<sub>3-γ</sub> as a product of the decomposition reaction (2). Composition of both cation and anion sublattice of this compound is expected to depend significantly on temperature and oxygen partial pressure in ambient gas atmosphere.

Overall electrical conductivity of YBaCo<sub>2</sub>O<sub>6-δ</sub> was measured as a function of  $pO_2$  at a given temperature in the range  $900 \leq T, ^\circ C \leq 1050$  with step of 50°C. The overall conductivity measured as a function of  $pO_2$  at different temperatures is shown in Figure 7. As seen in Figure 7, the overall conductivity first slightly decreases with  $pO_2$  descent in ambient atmosphere down to certain threshold value (around  $pO_2 = 10^{-2}, 10^{-3}, 10^{-3.5},$  and  $10^{-4}$  atm at 1050, 1000, 950, and 900°C, resp.), indicating in favor of electron holes as



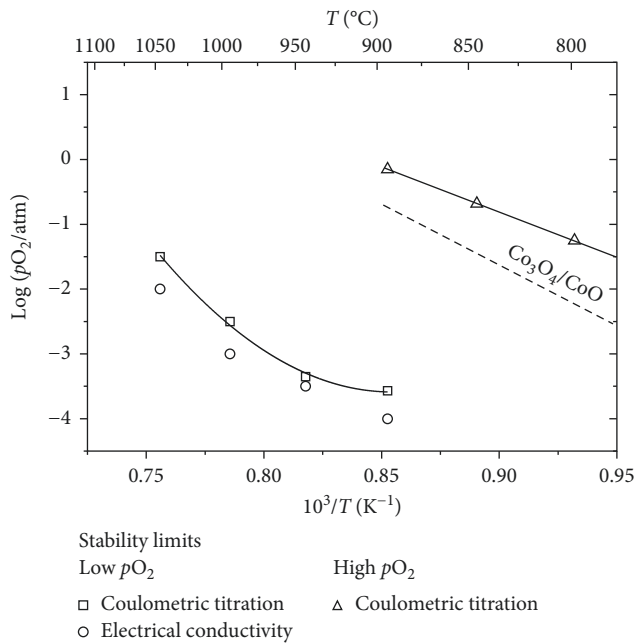


FIGURE 6: Thermodynamic stability limits of  $YBaCo_2O_{6-\delta}$ .

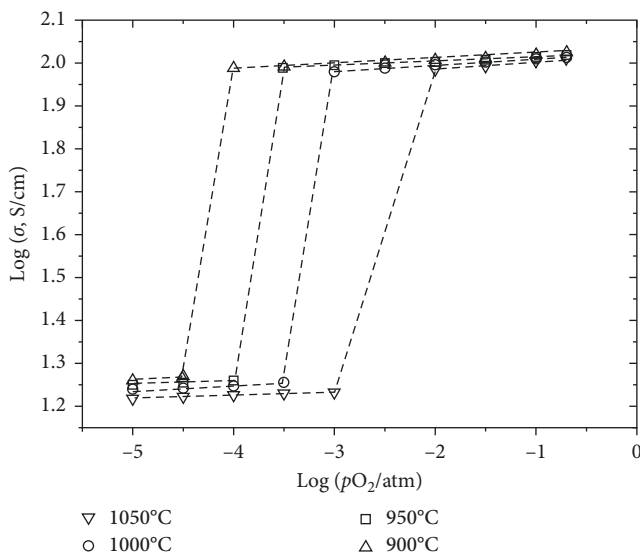


FIGURE 7: Overall conductivity of  $YBaCo_2O_{6-\delta}$  versus  $pO_2$  at different temperatures. Points correspond to experimental data and dash lines are guide to eye only.

dominant charge carriers, and then abruptly drops down on about an order of magnitude; afterwards it remains unchanged in practical term upon further  $pO_2$  decrease. Such conductivity drop observed at low  $pO_2$  at all temperatures studied in the present work is obviously related to the  $YBaCo_2O_{6-\delta}$  decomposition upon reaching the low  $pO_2$  stability limit.

For the sake of comparison, the values of  $pO_2$  at which the conductivity drop was observed are also given in Figure 6 depending on reciprocal temperature. As seen, the datasets

on stability obtained by means of different techniques are in agreement with each other pretty well.

In order to confirm the high  $pO_2$  stability limit, a single phase sample of  $YBaCo_2O_{6-\delta}$  was annealed at  $800^\circ C$  for 10 hours in air followed by quenching to room temperature. XRD of the so-prepared sample showed the presence of  $YCoO_3$  and  $BaCoO_{3-z}$ . On the other hand, annealing of equimolar mixture of  $YCoO_3$  and  $BaCoO_{3-z}$  for 72 hours under the same conditions was found not to lead to the formation of the double perovskite whilst it is formed in result of this mixture annealing at  $900^\circ C$  in air for the same time. These findings are in full coincidence with the stability diagram plotted (Figure 6) as well as with the data of the authors [15]. It follows from the stability diagram shown in Figure 5 that the double perovskite  $YBaCo_2O_{6-\delta}$  is thermodynamically stable in air only at  $850^\circ C$  and higher temperatures while it can be formed only as a metastable phase below this temperature. The last conclusion is in full agreement with the results of the paper by Zhang et al. [14] where  $YBaCo_2O_{6-\delta}$  was found to be stable at  $850^\circ C$  in air. The results of the thermodynamic stability investigation were further used to optimize the synthesis routine for  $YBaCo_2O_{6-\delta}$  as described elsewhere [29].

#### 4. Conclusion

The thermodynamic stability and oxygen nonstoichiometry of the double perovskite  $YBaCo_2O_{6-\delta}$  was studied using coulometric titration technique. The stability diagram of  $YBaCo_2O_{6-\delta}$  was plotted. The found limits of its thermodynamic stability were successfully verified by measurements of the overall conductivity as a function of oxygen partial pressure at given temperatures.  $YBaCo_2O_{6-\delta}$  was shown to be thermodynamically stable in the range of  $pO_2$  between certain threshold values at a given temperature likewise  $YBaCo_4O_{7\pm\delta}$  studied earlier [27]. For instance,  $YBaCo_2O_{6-\delta}$  was found to be thermodynamically stable in air at  $850^\circ C$  and higher temperatures, whereas its thermodynamic stability at  $900^\circ C$  is limited by the range of oxygen partial pressures  $-3.56 \leq \log(pO_2/atm) \leq -0.14$ . Oxygen content in  $YBaCo_2O_{6-\delta}$  was found to decrease slightly at  $900^\circ C$  from 5.035 at  $\log(pO_2/atm) = -0.14$  to 4.989 in the atmosphere with  $\log(pO_2/atm) = -3.565$ . Such narrow homogeneity region corresponds to a small change of the average oxidation state of cobalt; that is, even slight reduction of  $Co^{3+}$  or oxidation of  $Co^{2+}$  may result in  $YBaCo_2O_{6-\delta}$  oxide decomposition.  $YBaCo_2O_{6-\delta}$  decomposes into the mixture of  $YCoO_3$  and  $BaCoO_{3-z}$  at the high  $pO_2$  stability limit, whereas  $YBaCo_4O_7$ ,  $BaCo_{1-x}Y_xO_{3-y}$ , and  $Y_2O_3$  were identified as the products of its decomposition at the low  $pO_2$  one.

#### Conflicts of Interest

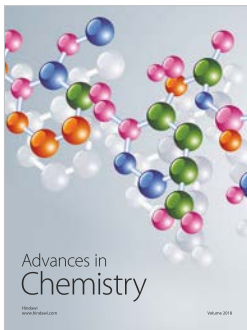
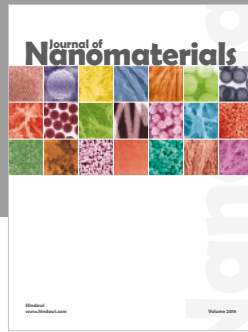
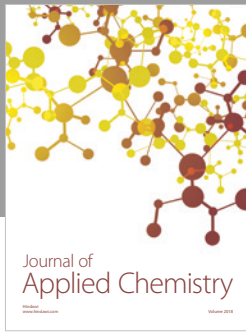
The authors declare that there are no conflicts of interest regarding the publication of this paper.

#### Acknowledgments

This work was supported by the Ural Federal University within the framework of Act 211 of Government of the Russian Federation, Agreement no. 02.A03.21.0006.

## References

- [1] R. Pelosato, G. Cordaro, D. Stucchi, C. Cristiani, and G. Dotelli, "Cobalt based layered perovskites as cathode material for intermediate temperature Solid Oxide Fuel Cells: a brief review," *Journal of Power Sources*, vol. 298, pp. 46–67, 2015.
- [2] A. A. Taskin, A. N. Lavrov, and Y. Ando, "Achieving fast oxygen diffusion in perovskites by cation ordering," *Applied Physics Letters*, vol. 86, no. 9, pp. 1–3, 2005.
- [3] M. Li, K. Chen, B. Hua et al., "Smart utilization of cobaltite-based double perovskite cathodes on barrier-layer-free zirconia electrolyte of solid oxide fuel cells," *Journal of Materials Chemistry A*, vol. 4, no. 48, pp. 19019–19025, 2016.
- [4] J.-H. Kim and A. Manthiram, "Layered  $\text{LnBaCo}_2\text{O}_{5+\delta}$  perovskite cathodes for solid oxide fuel cells: an overview and perspective," *Journal of Materials Chemistry A*, vol. 3, pp. 24195–24210, 2015.
- [5] D. S. Tsvetkov, I. L. Ivanov, D. A. Malyshev, and A. Y. Zuev, "Oxygen content, cobalt oxide exsolution and defect structure of the double perovskite  $\text{PrBaCo}_2\text{O}_{6-\delta}$ ," *Journal of Materials Chemistry A*, vol. 4, pp. 1962–1969, 2016.
- [6] J. Xue, Y. Shen, and T. He, "Double-perovskites  $\text{YBaCo}_{2-x}\text{Fe}_x\text{O}_{5+\delta}$  cathodes for intermediate-temperature solid oxide fuel cells," *Journal of Power Sources*, vol. 196, no. 8, pp. 3729–3735, 2011.
- [7] K. Zheng, K. Świerczek, J. Bratek, and A. Klimkowicz, "Cation-ordered perovskite-type anode and cathode materials for solid oxide fuel cells," *Solid State Ionics*, vol. 262, pp. 354–358, 2014.
- [8] R. Pelosato, A. Donazzi, G. Dotelli, C. Cinzia, I. N. Sora, and M. P. Mariani, "Electrical characterization of co-precipitated  $\text{LaBaCo}_2\text{O}_{5+\delta}$  and  $\text{YBaCo}_2\text{O}_{5+\delta}$  oxides," *Journal of the European Ceramic Society*, vol. 34, no. 16, pp. 4257–4272, 2014.
- [9] Y. Zhang, B. Yu, S. Lü et al., "Effect of Cu doping on  $\text{YBaCo}_2\text{O}_{5+\delta}$  as cathode for intermediate-temperature solid oxide fuel cells," *Electrochimica Acta*, vol. 134, pp. 107–115, 2014.
- [10] L. Yi, " $\text{YBaCo}_2\text{O}_{5+\delta}$  as a new cathode material for zirconia-based solid oxide fuel cells," *Journal of Alloys and Compounds*, vol. 477, no. 1-2, pp. 860–862, 2009.
- [11] J.-H. Kim and A. Manthiram, " $\text{LnBaCo}_2\text{O}_{5+\delta}$  oxides as cathodes for intermediate-temperature solid oxide fuel cells," *Journal of the Electrochemical Society*, vol. 155, pp. B385–B390, 2008.
- [12] F. Meng, T. Xia, J. Wang et al., "Evaluation of layered perovskites  $\text{YBa}_{1-x}\text{Sr}_x\text{Co}_2\text{O}_{5+\delta}$  as cathodes for intermediate-temperature solid oxide fuel cells," *International Journal of Hydrogen Energy*, vol. 39, no. 9, pp. 4531–4543, 2014.
- [13] X. Zhang, H. Hao, Q. He, and X. Hu, "High-temperature electronic transport properties of Fe-doped  $\text{YBaCo}_2\text{O}_{5+\delta}$ ," *Physica B: Condensed Matter*, vol. 394, no. 1, pp. 118–121, 2007.
- [14] K. Zhang, L. Ge, R. Ran, Z. Shao, and S. Liu, "Synthesis, characterization and evaluation of cation-ordered  $\text{LnBaCo}_2\text{O}_{5+\delta}$  as materials of oxygen permeation membranes and cathodes of SOFCs," *Acta Materialia*, vol. 56, no. 17, pp. 4876–4889, 2008.
- [15] J. H. Kim, Y. N. Kim, Z. Bi, A. Manthiram, M. P. Paranthaman, and A. Huq, "Overcoming phase instability of  $\text{RBaCo}_2\text{O}_{5+\delta}$  ( $R = \text{Y}$  and  $\text{Ho}$ ) by Sr substitution for application as cathodes in solid oxide fuel cells," *Solid State Ionics*, vol. 253, pp. 81–87, 2013.
- [16] H. Haoshan, Z. Lu, W. Yingfan, L. Shijiang, and H. Xing, "Thermogravimetric study on oxygen adsorption/desorption properties of double perovskite structure oxides  $\text{REBaCo}_2\text{O}_{5+\delta}$  ( $\text{RE} = \text{Pr}, \text{Gd}, \text{Y}$ )," *Journal of Rare Earths*, vol. 25, no. 3, pp. 275–281, 2007.
- [17] H. Hao, B. Chen, L. Zhao, and X. Hu, "Oxygen removal from nitrogen using  $\text{YBaCo}_2\text{O}_{5+\delta}$  adsorbent," *Korean Journal of Chemical Engineering*, vol. 28, no. 2, pp. 563–566, 2011.
- [18] D. S. Tsvetkov, V. V. Sereda, and A. Y. Zuev, "Oxygen nonstoichiometry and defect structure of the double perovskite  $\text{GdBaCo}_2\text{O}_{6-\delta}$ ," *Solid State Ionics*, vol. 180, no. 40, pp. 1620–1625, 2010.
- [19] A. Y. Zuev and D. S. Tsvetkov, "Conventional methods for measurements of chemomechanical coupling," in *Electro-Chemo-Mechanics of Solids*, S. R. Bishop, N. Perry, D. Marrocchelli, and B. Sheldon, Eds., Springer, Cham, Switzerland, 2017.
- [20] A. N. Petrov, A. Y. Zuev, and A. I. Vylkov, "The thermodynamic characteristics of point defects and the mechanism of electricity transfer in copper-containing lanthanum cobaltite  $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  ( $x=0.3$ )," *Russian Journal of Physical Chemistry*, vol. 79, pp. 173–178, 2005.
- [21] K. Knizek, Z. Jirak, J. Hejtmanek et al., "Structure and physical properties of  $\text{YCoO}_3$  at temperatures up to 1000 K," *Physical Review B*, vol. 73, p. 21444, 2006.
- [22] S. Balamurugan and E. Takayama-Muromachi, "Structural and magnetic properties of high-pressure/high-temperature synthesized  $(\text{Sr}_{1-x}\text{R}_x)\text{CoO}_3$  ( $R=\text{Y}$  and  $\text{Ho}$ ) perovskites," *Journal of Solid State Chemistry*, vol. 179, no. 7, pp. 2231–2236, 2006.
- [23] C. Felser, K. Yamaura, and R. J. Cava, "The electronic structure of hexagonal  $\text{BaCoO}_3$ ," *J. Solid State Chem*, vol. 146, no. 2, pp. 411–417, 1999.
- [24] P. M. Botta, V. Pardo, C. de la Calle, D. Baldomir, J. A. Alonso, and J. Rivas, "Ferromagnetic clusters in polycrystalline  $\text{BaCoO}_3$ ," *Journal of Magnetism and Magnetic Materials*, vol. 316, no. 2, pp. e670–e673, 2007.
- [25] A. S. Urusova, V. A. Cherepanov, T. V. Aksenova, L. Ya. Gavrilova, and E. A. Kiselev, "Phase equilibria, crystal structure and oxygen content of intermediate phases in the  $\text{Y-Ba-Co-O}$  system," *Journal of Solid State Chemistry*, vol. 202, pp. 207–214, 2013.
- [26] A. J. Jacobson and J. L. Hutchinson, "An investigation of the structure of  $12\text{H BaCoO}_{2.6}$  by electron microscopy and powder neutron diffraction," *Journal of Solid State Chemistry*, vol. 35, no. 3, pp. 334–340, 1980.
- [27] D. S. Tsvetkov, V. Pralong, N. S. Tsvetkova, and A. Y. Zuev, "Oxygen content and thermodynamic stability of  $\text{YBaCo}_4\text{O}_{7\pm\delta}$ ," *Solid State Ionics*, vol. 278, pp. 1–4, 2015.
- [28] A. Y. Zuev, "Oxygen nonstoichiometry, defect structure and related properties of perovskite-type oxides containing rare-earth, alkaline-earth and 3d-elements," Thesis for the degree of Doctor of Science in Chemistry, Ural Federal University, Ekaterinburg, Russia, 2011.
- [29] A. L. Sednev and D. S. Tsvetkov, "Study and optimization of the synthesis routine of the single phase  $\text{YBaCo}_2\text{O}_{6-\delta}$  double perovskite," *Chimica Techno Acta*, vol. 4, no. 3, pp. 183–190, 2017.



**Hindawi**  
Submit your manuscripts at  
[www.hindawi.com](http://www.hindawi.com)

