

Research Article

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

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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 YCoO_3 and BaCoO_{3-z} at the high $p\text{O}_2$ stability limit, whereas YBaCo_4O_7 , $\text{BaCo}_{1-x}\text{Y}_x\text{O}_{3-y}$, and Y_2O_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 YCoO_3 , BaCo_2O_3 , and $\text{YBaCo}_2\text{O}_{6-\delta}$ were synthesized by means of glycerol-nitrate technique using Co , Y_2O_3 , and BaCO_3 as starting materials. Y_2O_3 and BaCO_3 had a purity of 99.99%. Metallic Co was obtained by reduction of Co_3O_4 (purity 99.99%) in H_2 atmosphere at 600°C . Y_2O_3 and BaCO_3 were preliminary calcined in air at 1100°C and 600°C , respectively, for removal of adsorbed H_2O and 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 N_2 . The as-prepared solutions were heated continuously at 100°C until complete water evaporation and pyrolysis of the dried precursor had occurred. The resulting ash was subsequently calcined for 10 hours at 1100°C for BaCo_2O_3 as well as $\text{YBaCo}_2\text{O}_{6-\delta}$ and 900°C for 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°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 δ in $\text{YBaCo}_2\text{O}_{6-\delta}$ sample was determined by direct reduction by hydrogen flux in the TG setup (TG/H₂). 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 YCoO_3 and BaCo_2O_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°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°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 YCoO_3 , $\text{YBaCo}_2\text{O}_{6-\delta}$, and BaCo_2O_3 are given in Figures 1–3, respectively. It should be mentioned that the pattern of BaCo_2O_3 was interpreted as a mixture of two compounds BaCo_2O_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/H₂ (5.016 ± 0.002 at 900°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°C is shown in Figure 5.

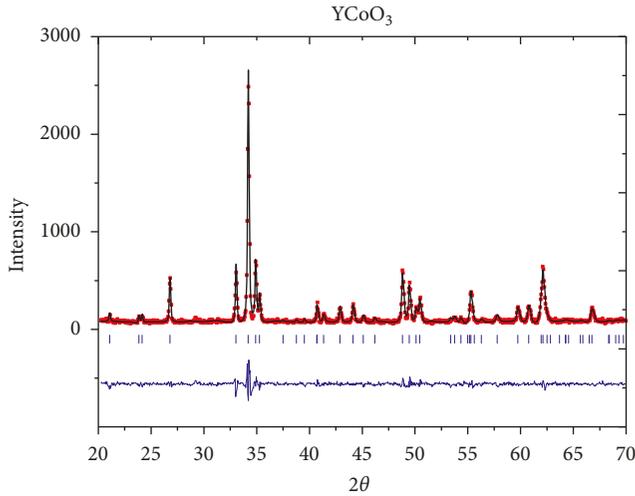
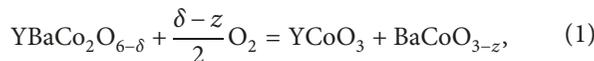


FIGURE 1: X-ray diffraction pattern and its matching refinement plot of YCoO_3 : observed X-ray diffraction intensity (points) and calculated curve (line). The bottom curve is the difference of patterns, $y_{\text{obs}} - y_{\text{cal}}$, and the small bars indicate the angular positions of the allowed 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°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 Co^{3+} or oxidation of Co^{2+} may result in $\text{YBaCo}_2\text{O}_{6-\delta}$ oxide decomposition. Coulometric measurements carried out at 900°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 YCoO_3 and the barium cobaltites 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°C up to 5.035 at 900°C . It is worth noting that reaction (1) is completely in line with the finding of the authors [15] that the perovskites

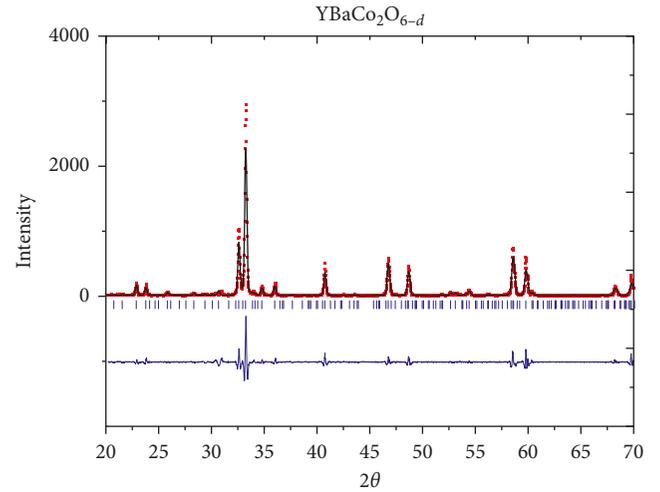


FIGURE 2: X-ray diffraction pattern and its matching refinement plot of $\text{YBaCo}_2\text{O}_{6-\delta}$: observed X-ray diffraction intensity (points) and calculated curve (line). The bottom curve is the difference of patterns, $y_{\text{obs}} - y_{\text{cal}}$, and the small bars indicate the angular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

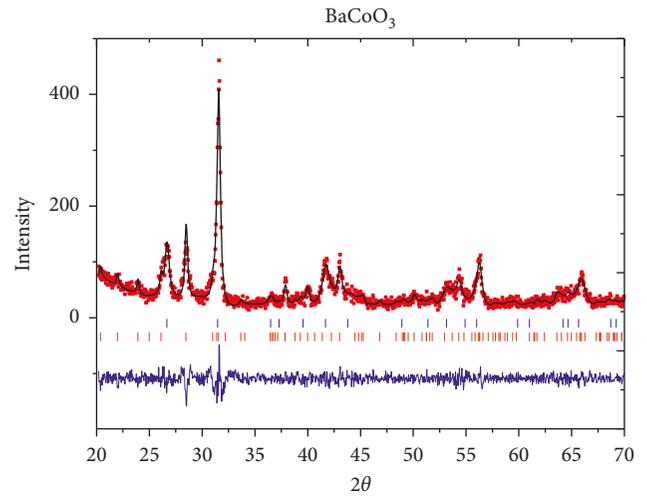


FIGURE 3: X-ray diffraction pattern and its matching refinement plot of BaCoO_3 , interpreted as a mixture of BaCoO_3 and $\text{BaCoO}_{2.61}$: observed X-ray diffraction intensity (points) and calculated curve (line). The bottom curve is the difference of patterns, $y_{\text{obs}} - y_{\text{cal}}$, and the small bars indicate the angular positions of the allowed Bragg reflections.

YCoO_3 and 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°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°C in gas atmosphere with $\log(p\text{O}_2/\text{atm}) = -4$ for 12 hours and then quenched to ice at -18°C . The XRD pattern of the sample prepared accordingly showed the presence of YBaCo_4O_7 , $\text{BaCo}_{1-x}\text{Y}_x\text{O}_{3-2z}$ and Y_2O_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 ₂ O _{6-δ}	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 ₃	Pbnm	5.139	5.419	7.365	Present work
		5.137	5.420	7.364	[21]
		5.132	5.411	7.360	[22]
BaCoO ₃	P-6m2	5.683	5.683	4.552	Present work
		5.645	5.645	4.752	[23]
		5.652	5.6525	4.763	[24]
		5.666	5.666	28.494	Present work
BaCoO _{2.63}	P63/mmc	5.665	5.665	28.493	[25]
		5.671	5.671	28.545	[26]

*Uncertainty ± 0.001 Å.

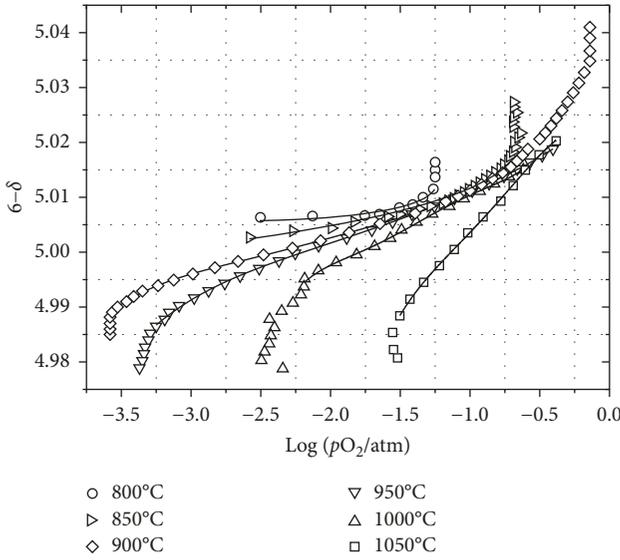
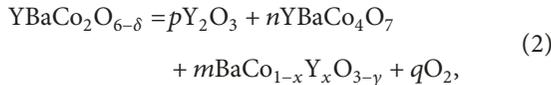


FIGURE 4: Oxygen content, $6-\delta$, in YBaCo₂O_{6-δ} versus pO_2 at different temperatures. Points correspond to experimental data and lines are guide to eye only.



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 YBaCo₄O₇ 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 $\log(pO_2/\text{atm}) = -3.5$ [27].

It is worth noting that decomposition of YBaCo₂O_{6-δ} is quite different from that of another double perovskite, for instance GdBaCo₂O_{6-δ}, which decomposes at low pO_2 according to completely different reaction [28]:

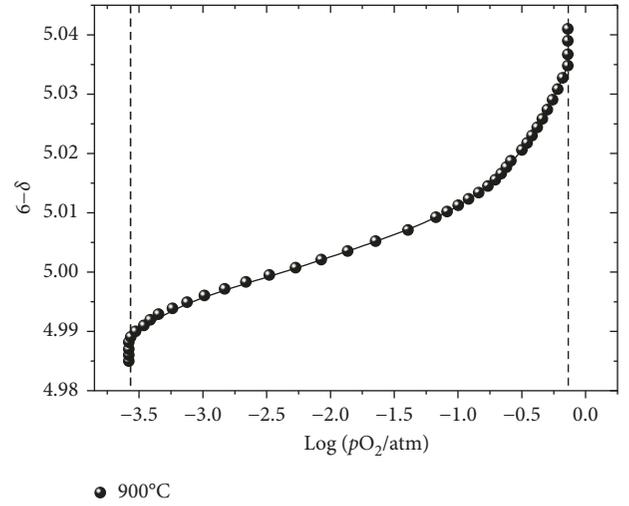
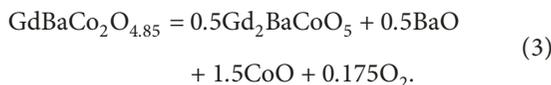


FIGURE 5: Oxygen content, $6-\delta$, in YBaCo₂O_{6-δ} versus pO_2 at 900°C. Points correspond to experimental data and line is guide to eye only.

Thermodynamic stability limits of YBaCo₂O_{6-δ} 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 YBaCo₂O_{6-δ} is related probably to a real composition of BaCo_{1-x}Y_xO_{3-γ} 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 YBaCo₂O_{6-δ} 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

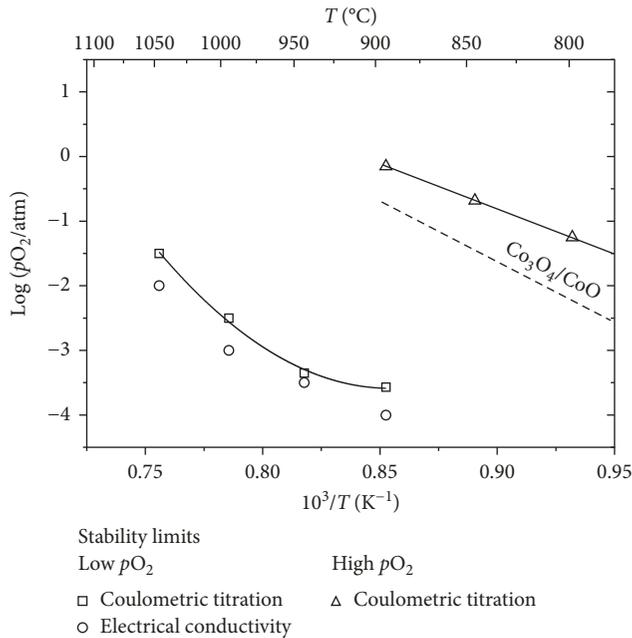


FIGURE 6: Thermodynamic stability limits of $\text{YBaCo}_2\text{O}_{6-\delta}$.

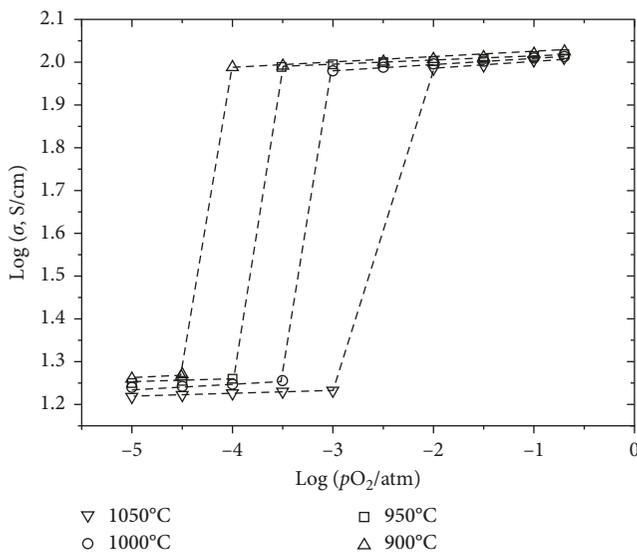


FIGURE 7: Overall conductivity of $\text{YBaCo}_2\text{O}_{6-\delta}$ versus $p\text{O}_2$ at different temperatures. Points correspond to experimental data and dash lines are guide to eye only.

dominant charge carriers, and then abruptly drops down on about an order of magnitude; afterwards it remains unchanged in practical term upon further $p\text{O}_2$ decrease. Such conductivity drop observed at low $p\text{O}_2$ at all temperatures studied in the present work is obviously related to the $\text{YBaCo}_2\text{O}_{6-\delta}$ decomposition upon reaching the low $p\text{O}_2$ stability limit.

For the sake of comparison, the values of $p\text{O}_2$ 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 $p\text{O}_2$ stability limit, a single phase sample of $\text{YBaCo}_2\text{O}_{6-\delta}$ was annealed at 800°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°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 $\text{YBaCo}_2\text{O}_{6-\delta}$ is thermodynamically stable in air only at 850°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 $\text{YBaCo}_2\text{O}_{6-\delta}$ was found to be stable at 850°C in air. The results of the thermodynamic stability investigation were further used to optimize the synthesis routine for $\text{YBaCo}_2\text{O}_{6-\delta}$ as described elsewhere [29].

4. Conclusion

The thermodynamic stability and oxygen nonstoichiometry of the double perovskite $\text{YBaCo}_2\text{O}_{6-\delta}$ was studied using coulometric titration technique. The stability diagram of $\text{YBaCo}_2\text{O}_{6-\delta}$ 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. $\text{YBaCo}_2\text{O}_{6-\delta}$ was shown to be thermodynamically stable in the range of $p\text{O}_2$ between certain threshold values at a given temperature likewise $\text{YBaCo}_4\text{O}_{7\pm\delta}$ studied earlier [27]. For instance, $\text{YBaCo}_2\text{O}_{6-\delta}$ 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 $\text{YBaCo}_2\text{O}_{6-\delta}$ was found to decrease slightly at 900°C from 5.035 at $\log(p\text{O}_2/\text{atm}) = -0.14$ to 4.989 in the atmosphere with $\log(p\text{O}_2/\text{atm}) = -3.565$. 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 $\text{YBaCo}_2\text{O}_{6-\delta}$ oxide decomposition. $\text{YBaCo}_2\text{O}_{6-\delta}$ decomposes into the mixture of YCoO_3 and BaCoO_{3-z} at the high $p\text{O}_2$ stability limit, whereas YBaCo_4O_7 , $\text{BaCo}_{1-x}\text{Y}_x\text{O}_{3-y}$, and Y_2O_3 were identified as the products of its decomposition at the low $p\text{O}_2$ one.

Conflicts of Interest

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

Acknowledgments

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