Phase equilibria, crystal structure and oxygen content of intermediate phases in the Y–Ba–Co–O system


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1. Introduction

The family of LnBaCo$_2$O$_{5+\delta}$ so-called double perovskites, in particular with Ln=Y, was intensively studied during last decade since they exhibit a set of properties such as high values of mixed electronic-ionic conductivity and oxygen mobility [1,2] that allows considering them as the promising cathode materials for the SOFCs [3]. Another representative of the Y–Ba–Co–O system that attracts attention of many researchers is YBaCo$_4$O$_{7+\delta}$ [4–7]. Although a number of papers were devoted to the structure and physicochemical properties of LnBaCo$_2$O$_{5+\delta}$ and YBaCo$_4$O$_{7+\delta}$, including the crystal structure and oxygen content [1–11] the information about phase equilibria in the YBa–Co–O system is absent. The only data that can be found has concern the phase formation in the quasibinary Y–Co–O, Y–Ba–O and Ba–Co–O systems.

1.1. Y–Co–O system

Only one complex oxide YCoO$_{3-\delta}$ was reported in the Y–Co–O system. It was prepared by standard ceramic technique under high (50–70 kbar) oxygen pressure [12], or at 1173 K during 100 h in the oxygen flow [13–15], or by the decomposition of yttrium and cobalt cyanides [16], or by sol–gel method [17,18]. According to X-ray diffraction it was found that after 120 h annealing at 1173 K YCoO$_{3-\delta}$ possesses orthorhombically distorted perovskite structure (sp.gr. Pbnm) [13–18]. The unit cell parameters presented by Jadhao et al. $a=5.132$ Å, $b=5.417$ Å, $c=7.367$ Å [16], were in good agreement with the data reported in [12,14,15]. According to Demazeau et al. [12] yttrium cobaltate YCoO$_{3-\delta}$ decomposes in air at temperature higher 1123 K, however synthesis conditions used in [13–15] make it possible to conclude that decomposition temperature probably exceeds 1173 K.

1.2. Y–Ba–O system

The phase diagram of the BaO–Y$_2$O$_3$ system in air has been studied by Lopato et al. [19], Kwestroo et al. [20] and Kovba et al. [21]. A number of ternary oxides were described in the system:
Y$_2$BaO$_4$ [19–21], Y$_4$Ba$_2$O$_9$ [19,20], Y$_2$Ba$_2$O$_5$ (Y$_2$Ba$_2$O$_{7.5}$) [20,21], Ba$_2$Y$_2$O$_5$ [20,21].

All authors found the existence of the Y$_2$BaO$_4$ from at least 900 °C [20,21] up to its solid state decomposition to the Y$_2$BaO$_4$ and Y$_2$O$_3$ at temperature about 1400 °C [19,21]. The Y$_2$Ba$_2$O$_5$ was reported to be stable from 1060 °C [21] up to its melting point at 2160 °C [19]. The thermal stability of the phase that is written as Y$_2$Ba$_2$O$_5$ [20] or Y$_2$Ba$_2$O$_{7.5}$ [21] has not exceeded 1040 °C. Ternary oxide with the formula Ba$_4$Y$_2$O$_7$ was found to be stable in the relatively narrow temperature range 1020–1140 °C [21]. This result do not agree with the data reported by Kwestroo et al. [20] that Ba$_4$Y$_2$O$_7$ had formed at 900 °C, and started to decompose at temperature above 1000 °C to the Y$_2$Ba$_2$O$_4$ and BaO. It was also mentioned that the stability of all phases in the BaO–Y$_2$O$_3$ system in the moist atmosphere is very poor and all of them decomposed immediately (except Y$_2$BaO$_4$) in moist air [20].

1.3. Ba–Co–O system

Two complex oxides Ba$_4$Co$_2$O$_9$ and BaCo$_2$O$_{4.5}$ [22–29] were described in the Ba–Co–O system at 1100 °C in air. Barium cobaltate BaCo$_2$O$_{4.5}$ synthesized by traditional ceramic method [22–27], or nitrate–route method [28] within the temperature range 600–1000 °C in air possesses hexagonal layered structure (sp. gr. $P6_3/mmc$). The alternation of layers along c-axis and oxygen content of BaCo$_2$O$_{4.5}$ strongly depend on the temperature and oxygen pressure used for preparation. Low temperature hexagonal (2H) structure [22] transformed into different polytypes, for example (5H) with 3–6 = 2.74 [25], or (12H) with 3–6 = 2.6 [26], while it lost oxygen with temperature increase or oxygen pressure decrease.

Another phase found to exist in this system in the temperature range 1063–1323 K was Ba$_2$Co$_3$O$_7$ [22,29] with the monoclinic structure $a = 5.8878(4)$ Å; $b = 7.6158(6)$ Å; $c = 10.3916(8)$ Å; $\beta = 90.738(2)$ [29].

This paper focuses on the phase equilibria in the Y–Ba–Co–O system at 1373 K in air and determination of the crystal structure of intermediate phases. Since the properties of the intermediate phases strongly depend on the oxygen content the changes of $\delta$ as a function of temperature were measured.

2. Experimental

The samples were prepared using a conventional ceramic and glycerol–nitrate techniques. In both methods yttrium oxide Y$_2$O$_3$ (with 99.99% purity), barium carbonate BaCO$_3$ and cobalt oxide Co$_2$O$_4$ (both of “pure for analysis” grade) and metallic cobalt were used as starting materials. Metallic cobalt was obtained by reducing of cobalt oxide in the hydrogen flow at 773–873 K during 6 h. After weighting the starting materials (oxides and barium carbonate) were preliminary annealed in order to remove adsorbed gases and water. Solid state synthesis was performed by stages within the temperature range 1123–1373 K in air with intermediate grindings in the agate mortar in alcoholic media. According to the glycerol nitrate technique yttrium oxide, barium carbonate and metallic cobalt taken in appropriate ratios were dissolved in nitric acid, and then glycerol in the amount needed for a complete reduction of nitrate ions was added. Then solution was dried to a viscous gel that further transformed to a powder while the temperature increasing. Finally this powder was annealed at 1373 K during 120–240 h with intermediate grindings. All samples for the phase equilibria study were quenched to room temperature with cooling rate about 500 K/min. The samples YBaCo$_2$O$_{5+\delta}$ and BaCo$_{1-y}$Y$_2$O$_{3-\delta}$ for the structural examination were slowly cooled from 1373 K (cooling rate about 100 K/h) in air.

X-ray diffraction of quenched or slowly cooled powder samples was performed at room temperature using diffractometer DRON-6 in Cu-K$\alpha$ radiation ($\lambda = 1.5418$ Å) with pyrolytic graphite monochromator within the angle range 10° ≤ 2$\Theta$ ≤ 120° (scan step 0.02 or 0.04 with the exposure time 2–10 s). The structural parameters were refined by the Rietveld profile method using the Fullprof-2008 package. The changes of oxygen content in the single phase complex oxides were measured by TGA method (STA 409PC, Netzsch Gmbh). The samples were placed in the TGA cell, heated up to 1373 K and equilibrated in air at this temperature during 10 h. The measurements were performed in the cooling and heating modes (cooling/heating rate 0.5–2/min).

The absolute values of oxygen content were determined using two methods.

(1) Iodometric titration. While dissolving the samples in dilute hydrochloric acid containing an excess of potassium iodide the following reduction–oxidation reaction is taking place:

$$2Co^{2+} + 3 \times (z-2)I^- \rightarrow 2Co^{3+} + (z-2)I_3^-$$

Since the oxygen content in the yttrium barium cobaltate can be linked with the mean oxidation state of cobalt ions Y$^{3+}$Ba$^{2+}$Co$^{2+}$O$_{z+\delta}$, it is possible to calculate it from the certain amount of iodine released in the reaction (1).

The amount of liberated iodine was determined by a titration with the sodium thiosulfate:

$$I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-}$$

The concentration of Na$_2$S$_2$O$_3$ was preliminary determined by a chromatometric titration using exact amount of K$_2$Cr$_2$O$_7$. In all cases the end points were obtained by using the automatic titration device (Avkilon ATP-02).

(2) Direct reduction of the samples in the TG cell by hydrogen (10% H$_2$–90% Ar) at 1373 K assuming Y$_2$O$_3$, BaO and metallic Co as final products.

Thermal expansion measurements were carried out within the temperature range 298–1373 K in air using the dilatometer (Netzsch Gmbh DIL 402C) at a heating/cooling rate of 5 K/min. The samples for the measurements were preliminary sintered into the form of the bar with the sizes about 3 × 3 × 25 mm at 1100 °C during 20 h.

3. Results and discussion

Phase equilibria in the Y–Ba–Co–O system were systematically studied at 1373 K in air.

3.1. “YCoO$_{3-\delta}$”–BaCoO$_{2-\delta}$ system

In order to study the nature of phases existing within the compositional range Y$_{1-x}$Ba$_x$CoO$_{3-\delta}$ (0 ≤ $x$ ≤ 1) the samples of appropriate compositions (x=0, 0.3, 0.5, 0.66, 0.8, 0.9 and 1) were prepared using standard ceramic and glycerol–nitrate techniques. According to the results of XRD the sample with x=0 consisted of Y$_2$O$_3$ and CoO as expected since YCoO$_{3-\delta}$ is usually prepared and investigated at temperatures that do not exceed 1173 K [13–17]. On the other side the sample with x=1 was single phase BaCoO$_{2-\delta}$ crystallized in hexagonal structure with the unit cell parameters $a = 5.665$ Å, $c = 28.493$ Å (sp. gr. $P6_3/mmc$) that was in good agreement with the results reported earlier [26]. The only intermediate phase formed in the Y$_{1-x}$Ba$_x$CoO$_{3-\delta}$ (0 ≤ x ≤ 1) system was YBaCo$_2$O$_{5+\delta}$ (x=0.5). All other samples were three phase mixtures consisted of: Y$_2$O$_3$,
YBaCo$_2$O$_{5+\delta}$ and YBaCo$_2$O$_{5+\delta}$ for $x=0.3$; YBaCo$_3$O$_{7+\delta}$ and BaCo$_1.5$Y$_0.5$O$_{3.5}$ with fixed composition $y$ (which will be described below) for $x=0.66$ and $0.8$; same BaCo$_1.5$Y$_0.5$O$_{3.5}$ (with fixed composition), YBaCo$_3$O$_{7+\delta}$ and BaCo$_{0.6}$Y$_{0.4}$O$_{3.4}$ for $x=0.05$.

The values of oxygen content for the sample YBaCo$_2$O$_{5+\delta}$ slowly cooled to room temperature obtained from the results of iodometric titration and TGA reduction were equal to $(5+\delta)=5.40 \pm 0.01$ and $(5+\delta)=5.41 \pm 0.05$, correspondingly. Obtained results perfectly coincide with each other and were in good agreement with the value reported by Kim et al. [1]. The values of oxygen content in the YBaCo$_2$O$_{5+\delta}$ versus temperature within the range 300–1323 K in air calculated from the TGA measurements varied from 5.41 to 5.04 (Fig. 1).

Fig. 2 demonstrates XRD patterns of the single phase YBaCo$_2$O$_{5.4}$. It was found to be tetragonal with the $3a_p \times 3a_p \times 2a_p$ superstructure ($P4/mmm$ space group, $a=11.616(1)$ Å, $c=7.494(1)$ Å), that is in good agreement with the data presented earlier [2,6].

High-temperature X-ray diffraction patterns for the YBaCo$_2$O$_{5+\delta}$ in the temperature range from 298 K up to 1073 K and $Pd_2=0.21$ atm are shown on Fig. 3. The results of the Rietveld refinement for the yttrium barium cobaltite YBaCo$_2$O$_{5+\delta}$ are presented in Table 1. Although the changes of oxygen content were significant no structural changes were observed in YBaCo$_2$O$_{5+\delta}$ within the temperature range studied.

Fig. 4 presents linear increase of the unit cell parameters and unit cell volume for the YBaCo$_2$O$_{5+\delta}$ sample with increasing temperature in air.

The relative thermal expansion ($\Delta L/L_0$) of the YBaCo$_2$O$_{5+\delta}$ ceramic sample also increases practically linearly with increasing temperature in the temperature range of 298–1273 K. The average thermal expansion coefficient (TEC) of double perovskite in the measured temperature range is about $13.8 \times 10^{-6}$, K$^{-1}$, which is close to the value reported by Liu [3].
3.2. YBaCo\(_4\)O\(_7\)

Complex oxide with the composition YBaCo\(_4\)O\(_7\) was synthesized by the standard ceramic technique. According to the results of XRD analysis the sample quenched from the 1373 K to room temperature was single phase. XRD pattern for the YBaCo\(_4\)O\(_7\) refined by the Rietveld method is shown in Fig. 5. The parameters of hexagonal unit cell: \(a = 6.299(1)\) Å, \(c = 10.240(1)\) Å (sp. gr. \(P6_3\)mc) are in good agreement with those reported by Tsipis et al. [5]. The refined atom coordinates are listed in the Table 2.

3.3. BaCo\(_{1-x}\)Y\(_x\)O\(_{3-\delta}\) system

According to Lomakov et al. [30] cobalt ions can be substituted by yttrium in BaCo\(_{3-\delta}\). We have checked the possibility of BaCo\(_{1-x}\)Y\(_x\)O\(_{3-\delta}\) phases formation at 1373 K in air. Thereto the samples within the composition range 0.0\(\leq x\leq 0.6\) with the step 0.1 were prepared using standard ceramic technique described in Section 2. According to the results of X-ray diffraction analysis the homogeneity range for the BaCo\(_{1-x}\)Y\(_x\)O\(_{3-\delta}\) solid solutions at studied conditions appears within 0.1\(\leq y\leq 0.4\) (Fig. 6). XRD pattern for all single phase samples were refined by Rietveld method within the cubic structure (\(Pm\_3m\) space group). As an example, Fig. 7 illustrates the results for the BaCo\(_{0.8}\)Y\(_{0.2}\)O\(_{3-\delta}\) oxide, and the values of the unit cell parameters for all single phase samples are listed in Table 3.

The changes of oxygen content in the BaCo\(_{1-x}\)Y\(_x\)O\(_{3-\delta}\) solid solutions with 0.1\(\leq y\leq 0.4\) were measured by means of thermogravimetric technique within the temperature range 298–1373 K.

### Table 1

<table>
<thead>
<tr>
<th>(T, K)</th>
<th>(a, \text{Å})</th>
<th>(c, \text{Å})</th>
<th>(V, (\text{Å})^3)</th>
<th>(R_b, %)</th>
<th>(R_p, %)</th>
<th>(R_m, %)</th>
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<td>298</td>
<td>11.629(1)</td>
<td>7.503(1)</td>
<td>1014.75(3)</td>
<td>1.34</td>
<td>2.03</td>
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<tr>
<td>673</td>
<td>11.703(1)</td>
<td>7.567(1)</td>
<td>1036.45(1)</td>
<td>2.04</td>
<td>3.14</td>
<td>12.50</td>
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<td>873</td>
<td>11.750(1)</td>
<td>7.585(1)</td>
<td>1047.31(1)</td>
<td>1.66</td>
<td>3.06</td>
<td>10.90</td>
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<tr>
<td>1073</td>
<td>11.791(1)</td>
<td>7.617(1)</td>
<td>1059.01(2)</td>
<td>2.17</td>
<td>2.58</td>
<td>12.20</td>
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</table>

### Fig. 4

Temperature dependences of the unit cell parameters for the YBaCo\(_{2}\)O\(_{3+\delta}\) sample in air.

### Fig. 5

X-ray diffraction pattern of YBaCo\(_4\)O\(_7\) oxide. Points represent the experimental data and the solid curve is the calculated profile. A difference curve is plotted at the bottom. Vertical marks represent the position of allowed Bragg reflections.
in air. The absolute values of oxygen content were determined using both methods: iodometric titration of the slowly cooled samples and reduction in the TGA cell by hydrogen. Results obtained in a number of parallel experiments by both methods were in good agreement. For example, the value of oxygen content for BaCo$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ determined by the TGA was equal to 2.530 $\pm$ 0.005 and that obtained by iodometric titration--2.50 $\pm$ 0.04.

Temperature dependencies of the oxygen content in the Ba-Co$_{1-y}$Y$_y$O$_{3-\delta}$ single phase samples are shown in the Fig. 9. The shape of the dependencies for the samples with $y=0.1$ and 0.2 are similar to each other but differ from those for the samples with $y=0.3$ and 0.4 (which in turn were similar to each other as well), especially at temperature higher than $\sim$600 K. However all curves reveal bends at temperatures about 590 and 790--820 K. The nature of first bend for the temperature dependencies of oxygen content can be explained as starting of oxygen exchange between gaseous phase and

### Table 2

Refined atomic coordinates and reliability factors for the YBaCo$_4$O$_7$. (sp. gr. P6$_3$mc).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Y</th>
<th>Ba</th>
<th>Co1</th>
<th>Co2</th>
<th>O1</th>
<th>O2</th>
<th>O3</th>
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<tr>
<td>$x$</td>
<td>0.6667</td>
<td>0.6667</td>
<td>0.0000</td>
<td>0.1720(1)</td>
<td>0.5130(1)</td>
<td>0.0000</td>
<td>0.1680(1)</td>
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<tr>
<td>$y$</td>
<td>0.3333</td>
<td>0.3333</td>
<td>0.0000</td>
<td>0.8280(1)</td>
<td>0.4870(1)</td>
<td>0.0000</td>
<td>0.8320(1)</td>
</tr>
<tr>
<td>$z$</td>
<td>0.8700</td>
<td>0.5000</td>
<td>0.4310(1)</td>
<td>0.6880(1)</td>
<td>0.7430(1)</td>
<td>0.2430</td>
<td>0.5040(1)</td>
</tr>
</tbody>
</table>

$R_B=1.06\%$, $R_f=2.18\%$, $R_p=5.5\%$

![Fig. 6. X-ray diffraction pattern of BaCo$_{1-y}$Y$_y$O$_{3-\delta}$ solid solutions.](image)

![Fig. 7. X-ray diffraction pattern of BaCo$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ oxide. Points represent the experimental data and the solid curve is the calculated profile. A difference curve is plotted at the bottom. Vertical marks represent the position of allowed Bragg reflections.](image)

![Fig. 8. The dependence of the unit cell parameters for the BaCo$_{1-y}$Y$_y$O$_{3-\delta}$ solid solutions versus yttrium content.](image)

### Table 3

Unit cell parameters and reliability factors for the BaCo$_{1-y}$Y$_y$O$_{3-\delta}$ solid solutions (space group: Pm3m).

<table>
<thead>
<tr>
<th>$y$</th>
<th>$a$, Å</th>
<th>$V$, (Å$^3$)</th>
<th>$R_B$, %</th>
<th>$R_f$, %</th>
<th>$R_p$, %</th>
</tr>
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<td>0.1</td>
<td>4.106(1)</td>
<td>69.23(1)</td>
<td>1.44</td>
<td>1.24</td>
<td>14.70</td>
</tr>
<tr>
<td>0.15</td>
<td>4.123(1)</td>
<td>70.09(1)</td>
<td>0.65</td>
<td>0.51</td>
<td>8.69</td>
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<tr>
<td>0.2</td>
<td>4.136(1)</td>
<td>70.76(1)</td>
<td>1.76</td>
<td>1.60</td>
<td>10.10</td>
</tr>
<tr>
<td>0.3</td>
<td>4.168(1)</td>
<td>72.41(1)</td>
<td>0.93</td>
<td>1.23</td>
<td>9.25</td>
</tr>
<tr>
<td>0.4</td>
<td>4.195(1)</td>
<td>73.85(1)</td>
<td>0.87</td>
<td>1.59</td>
<td>11.30</td>
</tr>
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</table>
3.4. Phase equilibria in the Y–Ba–Co–O system

Overall phase equilibria in the Y–Ba–Co–O system were analyzed based on the results of XRD of 50 quenched samples. Phase relations at fixed temperature and oxygen pressure in a quaternary system (Y–Ba–Co–O) can be represented using a tetrahedron. A more convenient, planar representation can be obtained using the method of cross-sections. This method, however, is inapplicable to the system under consideration because the oxidation states of cobalt ions that various coexisted phases contain vary at the studied conditions, therefore the compositions of simple oxides and the compositions of the products do not lie in the same plane. For this reason, we used projection onto the plane of metallic components, an approach often used to represent such systems. In this respect the composition in the phase triangles is equal to the thermodynamically equilibrium value and could not be calculated from the composition triangle. The compositions of condensed phases in each point of a projection is assumed to be equal to the thermodynamically equilibrium value and could not be calculated from the composition triangle. The compositions of the samples taken into account are represented as points in the phase diagram (Fig. 13). As a result the phase triangle for the Y–Ba–Co–O system was divided into 14 fields.

Although we have not performed detailed systematic reinvestigation of phase equilibria in the BaO–Y2O3 system a number of samples were prepared in order to check the existence of phases described earlier [20–22]. X-ray diffraction of quenched from the 1100°C Y-rich samples (\( \xi > 0.6 \)) confirmed the existence of Y2BaO4 phase. Since barium oxide at room temperature easily reacts with the vapor in moist atmosphere and CO2 contained in air we have performed high temperature XRD measurement for these samples. It was shown that the phase Y2BaO4 can be obtained at 1100°C, while Y2Ba2O6 had not been stable at least at 1100°C. As an example X-ray diffraction pattern for the sample with composition corresponding to the point inside the field 7 (Fig. 13) has shown in Fig. 14.

It should be noted that no systematic study of melt region has been performed in the present work. The field (14) with partially

the crystal lattice. The nature of the second bend is not so obvious, but probably connected with a peculiarity of crystal structure changes with the oxygen content variations. It is also obvious that if at temperature below 600 K the values of oxygen content steadily decrease while the yttrium amount increases this dependency disappears at temperatures higher than 1100 K. However the values of mean oxidation state of Co ions versus temperature (Fig. 10), calculated from the electroneutrality conditions using the values of oxygen content look more consistent with respect to the changes of Y content. Another interesting observation of these data can be presented as the isothermal dependencies of mean oxidation state of Co ions versus Y content in the BaCo1−\( Y\)O3 samples (Fig. 11). One can see that at high temperatures (1200–1350 K) in the middle part of homogeneity range an increase of the Y content does not lead to the changes in oxidation state of Co ions, but is compensated by the variations in oxygen content.

Thermal expansion of BaCo1−\( Y\)O3 (\( Y = 0.0; 0.1; 0.2; 0.3 \)) samples was studied within the temperature range 298–1200 K in air (Fig. 12).

Monotonous shape of \( \Delta L/L = f(T) \) curves proves absence of phase transitions within studied temperature range in air. The break at 1200 K is observed on thermal expansion curve of BaCoO3 sample, which could be associated with structural changes.

The average TEC values for BaCo1−\( Y\)O3 are given in Table 4. It is seen that TEC values decreased with increasing of yttrium content. This tendency can probably be explained by the decrease of cobalt content that causes the decrease of the oxygen exchange capacity of the samples (Fig. 9).
or completely melted samples is shown schematically in the phase triangle.

4. Conclusions

The phase equilibria in the Y–Ba–Co–O system at 1373 K in air are presented in the form of isothermal isotopic projection to the compositional triangle. According to the results of XRD the intermediate phases formed in the Y–Ba–Co–O system at 1373 K

\[
\text{YBaCo}_2O_5 + \delta \text{YBaCo}_4O_7 \text{ and } \text{BaCo}_1 - y \text{Y}_y O_3 - \delta (0.09 \leq y \leq 0.42). \text{YBaCo}_2O_5 + \delta \text{ possesses tetragonal structure with the } 3\ap/c2\ap/c2\ap/\text{super}cell (\text{sp. gr. } P4/mmm). \text{The value of oxygen content in the } \text{YBaCo}_2O_5 + \delta \text{ has changed from } 5.40 \text{ at room temperature to } 5.04 \text{ at } 1323 K. 
\]

The formation of \text{BaCo}_1 - y \text{Y}_y O_3 - \delta \text{ solid solution with the cubic structure (sp. gr. } Pm3m) \text{ within the compositional range } 0.09 \leq y \leq 0.42 \text{ was detected. It was shown that increasing of yttrium content leads to a gradual decreasing of oxidation state of Co ions although at relatively high temperature this decrease is not monotonous.