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Thermochimica Acta 284 (1996) 367–378

thermochimica
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Thermal reactivity of the Co-substituted perovskite-related phase $\text{YBaFeCuO}_{5+\delta}$

T. Rentschler *

*Institute of Inorganic and Applied Chemistry, University of Hamburg, Martin-Luther-King-Platz 6,
20146 Hamburg, Germany*

Received 16 October 1995; accepted 24 November 1995

Abstract

The thermal reactivity of the perovskite-related phase YBaFeCuO_5 with a partial substitution of Fe or Cu by Co was investigated by applying different reactive gas atmospheres. The degradation of the structure under reducing conditions ($5\% \text{H}_2/\text{N}_2$) depends on the composition of the samples including mixed valences attributed to Co(II)/Co(III). From powder X-ray diffractometry of the decomposed product of $\text{YBaCoCu}_{0.6}\text{Fe}_{0.4}\text{O}_{5+\delta}$, a selective reduction of Co, Cu and the formation of a new ternary phase were detected. The reduction products easily reformed a perovskite phase under O_2 , as shown by TG DTA and XRD. Moreover, thermogravimetric studies proved the reversible incorporation and release of oxygen into the oxygen-deficient layered perovskite structure. An application for catalytical purposes is suggested.

Keywords: Perovskite; Reversible oxygen incorporation; Thermal reactivity; Thermogravimetry

1. Introduction

Metal oxides adopting perovskite-related structures are among the best investigated and most versatile compounds with respect to their chemical and physical properties. The possibility of achieving numerous metal cation combinations and stabilizing oxygen-deficient phases with ordered structures opens a large field for possible variations of their ceramic properties relevant for optics, magnetism, and conductivity, as well as for catalysis, sensors and electrodes.

* Tel.: + 49 40 4123 4290; Fax.: + 49 40 4123 6348.

As a representative of these structures, having recently gained considerable interest in the understanding of the superconductivity of the structurally parent high- T_c superconductors, the composition $\text{YBaFeCuO}_{5+\delta}$ exhibits a perovskite superstructure with a highly ordered two-dimensional vacancy distribution. The structure of $\text{YBaFeCuO}_{5+\delta}$ consists of corner-sharing CuO_5 and FeO_5 pyramids with Ba^{2+} in the regularly 12-fold coordinated perovskite positions and Y^{3+} in the oxygen-deficient layer between the basal planes of the $(\text{Fe}, \text{Cu})\text{O}_5$ pyramids [1]. A detailed discussion of the structure is given in Refs. [2, 3].

Within this structure, the B-cations Cu and Fe were successfully substituted by Co, leading to three groups of Co-doped materials: $\text{YBaFeCu}_{1-x}\text{Co}_x\text{O}_{5+\delta}$, $\text{YBaFe}_{1-x}\text{Co}_x\text{CuO}_{5+\delta}$ and $\text{YBaCoCu}_{1-x}\text{Fe}_x\text{O}_{5+\delta}$ [4]. This study focusses on the thermochemical reactivity of these perovskite-related phases. The application of TG – DTA under different atmospheres is of special interest since all the B-cations, Cu, Fe and Co, adopt different oxidation states in solids, including mixed valences. Under the influence of different reactive gases, changes in the oxidation states of the B-cations may be achieved due to the stabilizing effects of vacancies in the perovskite structure and/or a complete decomposition of the structural framework. In both cases, subsequent reversible reformation of the structure is possible in oxidizing atmospheres with respect to the reincorporation of oxygen into the vacancy sites and/or topochemical processes rebuilding the original structure.

An important feature is the reversibility of the thermochemical processes, including the variability of the oxygen stoichiometry through the redox-active cations in mixed valences. This suggests a possible application in redox-catalysed processes, with the option of adjusting the properties of the catalyst via different ratios of substitution of Co for Cu or Fe.

2. Experimental

All samples of the three systems $\text{YBaFeCu}_{1-x}\text{Co}_x\text{O}_{5+\delta}$, $\text{YBaFe}_{1-x}\text{Co}_x\text{CuO}_{5+\delta}$ and $\text{YBaCoCu}_{1-x}\text{Fe}_x\text{O}_{5+\delta}$, with $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0 , were prepared by solid state reaction as described in Ref. [4]. Structural studies of the samples, as well as of the products of thermal treatments, were performed by powder X-ray diffraction (XRD) using a Siemens D5000 diffractometer (Cu $K\alpha$ radiation, SiO_2 standard, PSD). Thermoanalytical measurements were carried out on a Netzsch STA 409 coupled to a quadrupole mass spectrometer (Balzers QMG 421). The experiments were performed under different gas atmospheres of pure oxygen or of forming gas (5% H_2/N_2) with a flow rate of 0.02 l min^{-1} at atmospheric pressure. The temperature was raised up to 800°C using a heating rate of 3 K min^{-1} . All thermogravimetric curves were corrected for buoyancy.

3. Results and discussion

For the three groups of materials, selected samples of each system were chosen for thermal analysis.

In the system $\text{YBaFeCu}_{1-x}\text{Co}_x\text{O}_{5+\delta}$ with a partial substitution of Cu by Co, the composition $\text{YBaFeCu}_{0.4}\text{Co}_{0.6}\text{O}_{5+\delta}$ was investigated. Fig. 1 illustrates the results of thermogravimetric measurements in different gas atmospheres. Under the influence of forming gas (5% H_2/N_2) the sample shows a stepwise reduction mechanism with increasing temperature. The two steps in the range 300–550°C and 550–800°C were accompanied by a mass loss of 1.2% equivalent to 0.3 mol oxygen per formula unit ($-\text{O}_{0.3}$) for each step. For higher temperatures, a quasi-continuous degradation of the structure is observed by TG and verified by XRD [4].

As a volatile product of reduction, H_2O is detected by the mass spectrometer whenever a mass loss occurred in TG.

Reheating the reduced product in pure oxygen is accompanied by an exothermic process with an uptake of oxygen of 2.9% (corresponding to $+\text{O}_{0.76}$) in the range 340–400°C (Fig. 1b). This oxidation process, which takes place at the temperature

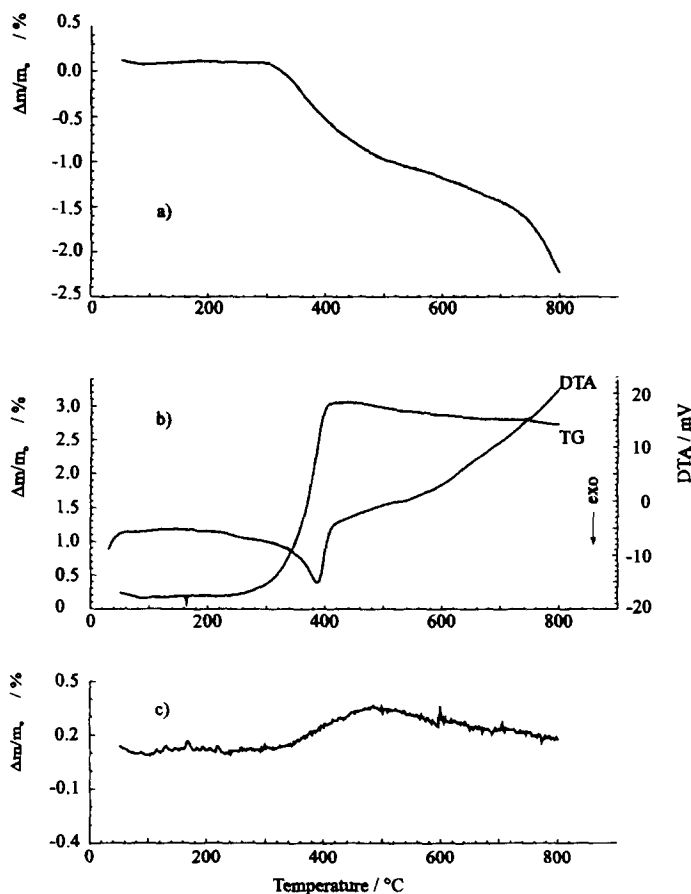


Fig. 1. Thermogravimetric measurements of $\text{YBaFeCu}_{0.4}\text{Co}_{0.6}\text{O}_{5+\delta}$: (a) in 5% H_2/N_2 ; (b) reoxidation of the reduced product from (a) including DTA in pure oxygen; and (c) TG of the as-prepared powder with O_2 .

where the first step of reduction occurred, refers to the reformation of the perovskitic structure according to the exothermic DTA signal and powder X-ray diffraction of the product. Thus the temperature range 340–400°C corresponds to the beginning of thermochemical processes for this perovskitic phase, i.e. the reactivity of redox-active cations may be related to the onset of oxygen mobility through the lattice. While the stepwise reduction can be interpreted by the formation of an intermediate, stabilized phase of a lower oxygen content with a subsequent degradation above 700°C, the complete reoxidation forming the thermodynamically favourable perovskite is obtained in one step as soon as the temperature for the thermochemical oxidation process is reached.

As this reoxidation required a little more oxygen compared to the mass loss during reduction, a partial oxidation of Co(II) to Co(III) including the incorporation of additional oxygen on the vacancy sites of the structure might have occurred. However, a comparison of these effects or of their minor differences is within the experimental error limit.

However, heating the as-prepared powder in flowing oxygen atmosphere results in only a 0.2% mass gain (+ O_{0.05}) as observed by TG between 360 and 500°C, pointing to a partial oxidation of cobalt as demonstrated in Fig. 1c. However, for still higher temperatures, this additional oxygen was again released slowly according to TG, an effect which was also observed in the system YBaCoCu_{1-x}Fe_xO_{5+δ}. Within this range of temperature, YBaFeCu_{0.4}Co_{0.6}O_{5+δ} might act as a possible catalyst for oxidative processes, since to a certain extent it can reversibly incorporate and release oxygen from the lattice due to mixed valences of the B-cations and structural stabilization of different vacancy-ordering schemes.

In the second group of materials, YBaFe_{1-x}Co_xCuO_{5+δ}, Fe is partially substituted by Co. In contrast to the previous sample, Co is formally incorporated as Co(III). For a comparison with the first system, the sample YBaFe_{0.4}Co_{0.6}CuO_{5+δ} was chosen, having an identical Co content. The thermogravimetric analysis under 5% H₂/N₂ or O₂, respectively, are shown in Fig. 2. The reduction in 5% H₂/N₂ is observed between 400 and 660°C with a mass loss of 2.2% (- O_{0.6}). The progress of reduction is basically comparable to the sample YBaFeCu_{0.4}Co_{0.6}O_{5+δ}, although the two steps are less pronounced because the reduction starts at higher temperatures (380°C) and the second step begins earlier (500°C), so that the reaction is basically completed at 660°C.

On heating the as-prepared powder in flowing oxygen, no changes were detected by TG up to 800°C concerning a possible oxidation of different cations (Fig. 2b). Therefore it might be concluded that Co is indeed incorporated as Co(III) into the perovskite phase. Moreover, no oxygen loss of the sample was detected at higher temperatures. In contrast to the characterized samples of the other two groups of materials, YBaFe_{0.4}Co_{0.6}CuO_{5+δ} exhibited a completely inert behaviour between room temperature and 800°C. Thus this system can probably be ruled out for catalytic purposes as no indications for a redox-active system were found.

For the third group of materials, YBaCoCu_{1-x}Fe_xO_{5+δ}, various samples of different compositions were investigated.

The thermal analysis of the powder of formal stoichiometry YBaCoCu_{0.6}Fe_{0.4}O_{5+δ} is shown in Fig. 3. Under reducing conditions in 5% H₂/N₂, degradation of the sample

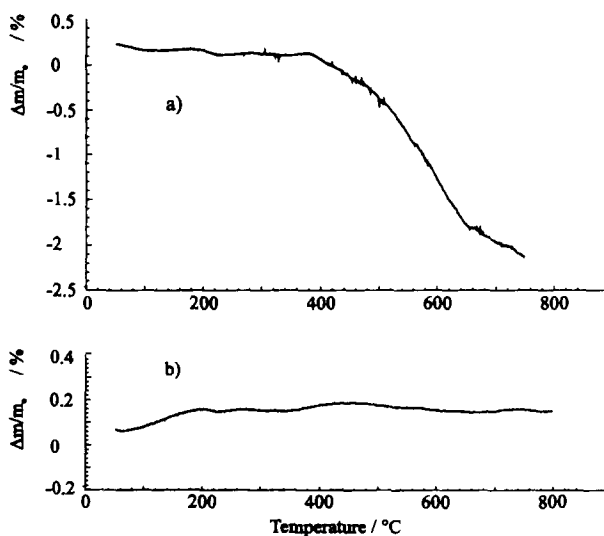


Fig. 2. Thermogravimetric measurements of $\text{YBaCuFe}_{0.4}\text{Co}_{0.6}\text{O}_{5+\delta}$: (a) under 5% H_2/N_2 and (b) in oxygen atmosphere.

in two steps is observed by TG and DTG. The first step, ranging from 300 to 640 $^{\circ}\text{C}$, can be correlated with a mass loss of 4.4% ($-\text{O}_{1.1}$), while another loss of 2.3% ($-\text{O}_{0.6}$) is followed with increasing temperature up to 800 $^{\circ}\text{C}$. Powder X-ray diffraction of the product reveals a complete degradation of the perovskite-related structure (see Fig. 4d) compared to the initial structure of the as-prepared powder in Fig. 4a. Attempts were made to isolate the product of the first step of reduction by heating the sample up to 650 $^{\circ}\text{C}$ and keeping at that temperature for 3 h, or by simply raising the temperature to 650 $^{\circ}\text{C}$ with subsequent cooling in 5% H_2/N_2 atmosphere. In the first case, according to XRD a complete decomposition of the structure occurred (Fig. 4c), equivalent to the initial experiment up to 800 $^{\circ}\text{C}$ (Fig. 4d), while in the second case only a partial reduction was observed (Fig. 4b).

The X-ray diagram of the product was analysed by a comparison with standard files of the ICDD database [5]. The reflections of the decomposed sample could be assigned to a multiphase system consisting of Y_2O_3 , $\text{Ba}_3\text{Fe}_2\text{O}_6$, Co, Cu and possible traces of Cu_2O . Consequently, under the applied reducing conditions Co and Cu were subjected to a metal-selective reduction, while the other metals formed a simple oxide or a new ternary phase. The overall reduction up to 800 $^{\circ}\text{C}$ corresponds to an oxygen loss of $\text{O}_{1.78}$ sufficient for a complete reduction of Cu and Co. However, on account of an assumed superposition of different effects during reductive processes, sustainable propositions on the mechanism of decomposition are limited.

The mass loss of 6.7% up to 800 $^{\circ}\text{C}$ is much larger compared to those the samples of the other two groups of materials (2.2%–2.4%). From this, it can be concluded that $\text{YBaCoCu}_{0.6}\text{Fe}_{0.4}\text{O}_{5+\delta}$ is thermodynamically less stable than the previous samples. This might be explained by the simultaneous formation of the new ternary oxide

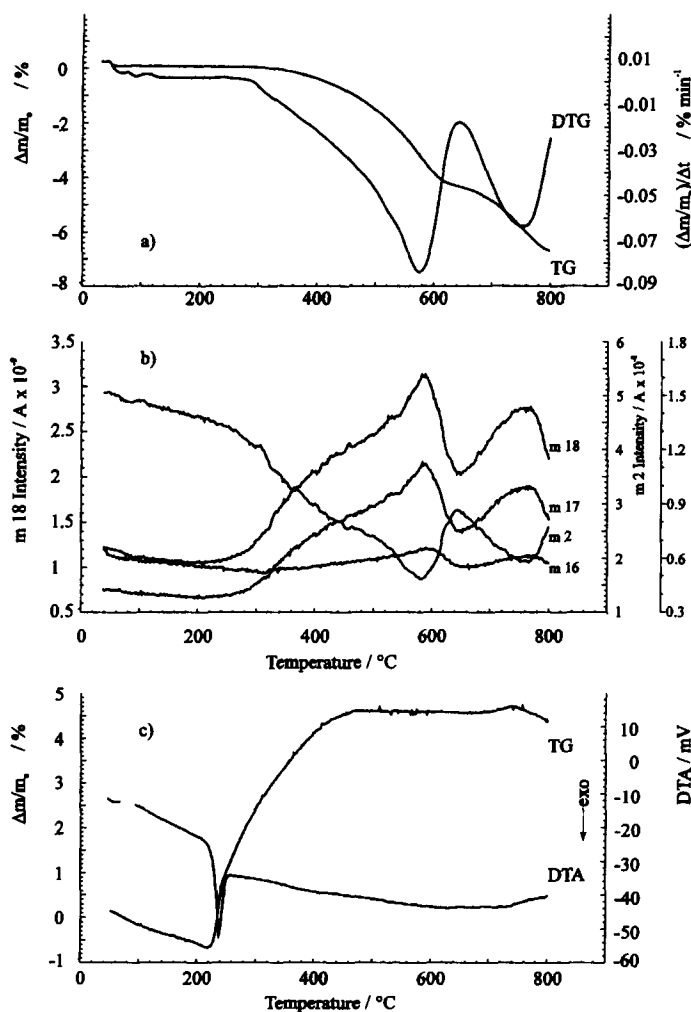


Fig. 3. (a) TG and DTG of $\text{YBaCoCu}_{0.6}\text{Fe}_{0.4}\text{O}_{5+\delta}$ in 5% H_2/N_2 ; (b) mass spectrometry of the carrier gas atmosphere; the intensity of H_2 (m 2) from the reactive carrier gas decreases whenever reduction of the oxide occurs by the formation of H_2O (m 18, 17, 16); (c) reoxidation of the reduced product with O_2 as observed by TG and DTA.

energetically favouring the overall reaction. As a consequence, the reactivity is not only controlled by the decomposition, i.e. by the metal-selective reduction of Co and Cu, but also by the possibility of forming new thermodynamically stable systems. For this reason, the thermochemical reactivity of the sample is strongly influenced by the variation in the stoichiometric ratios of the metals leading to possible new products during thermal treatment in various atmospheres.

Fig. 3b illustrates the signals of the coupled mass spectrometer recorded while heating the sample. With increasing temperature in forming gas, a reduction of the

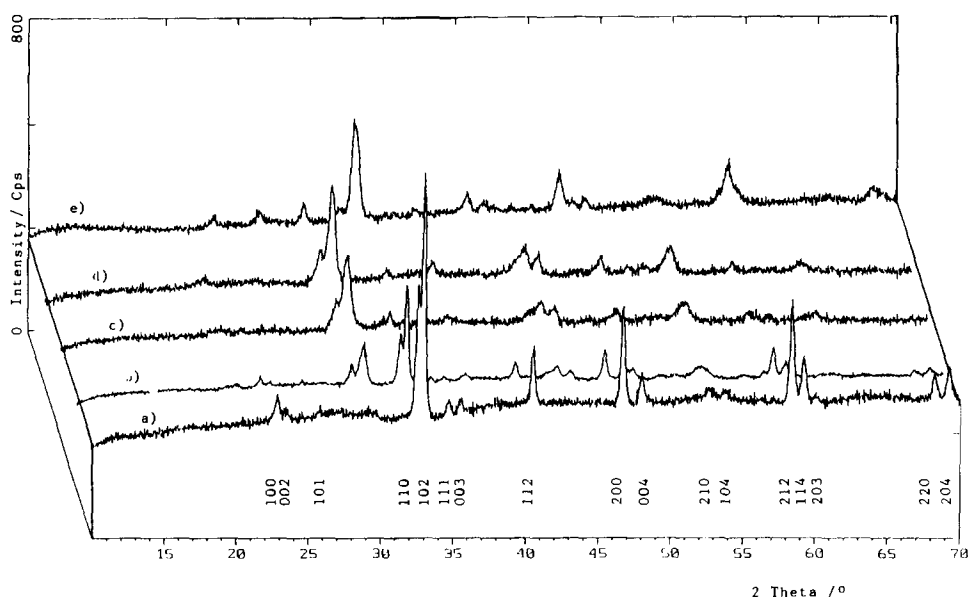


Fig. 4. Powder X-ray diffraction of $\text{YBaCoCu}_{0.6}\text{Fe}_{0.4}\text{O}_{5+\delta}$ from: (a) the as-prepared sample and after thermal analysis up to (b) 650°C, (c) 650°C for 3 h, (d) 800°C under 5% H_2/N_2 ; (e) reformation of the perovskite structure after heating in pure oxygen up to 800°C.

metal oxide takes place leading to the evolution of water (m_{18} , m_{17} , m_{16}) as volatile product. At the same time, the intensity of hydrogen (m_2) of the reactive carrier gas (5% H_2/N_2) drops proportionally to the formation of H_2O . The progress of these peaks corresponds exactly to the measured curves of TG and DTG shown in Fig. 3a. The start of the reduction is located by both methods at 300°C. The DTG minima occur at 580 and 760°C, exactly corresponding to the maxima of the peaks derived from the formation of H_2O as well as to the minima of the hydrogen content in the carrier gas atmosphere.

The reduction product was subjected to heating in pure oxygen up to 800°C with a simultaneous recording of TG and DTA as shown in Fig. 3c. The reaction starts at 220°C with a sharp maximum of the exothermic DTA peak from the reformation of a perovskite phase at 240°C. The overall oxygen uptake was 5.3% ($+ \text{O}_{1.4}$). The characterization of the product by XRD confirms the reformation of a perovskite phase (see Fig. 4e). The observed broadening of the reflections may be due to a particle size effect and/or to microscopic fluctuations of the chemical composition. This synthesis at a very low temperature might be explained in terms of a topotactical or topochemical reaction with the building blocks of the metal components already performed.

For the sample with nominal composition $\text{YBaCoCu}_{0.4}\text{Fe}_{0.6}\text{O}_{5+\delta}$, a similar thermochemical behaviour was observed in comparison with the previous sample $\text{YBaCoCu}_{0.6}\text{Fe}_{0.4}\text{O}_{5+\delta}$. The results of thermochemical analyses in different gas atmospheres are illustrated in Fig. 5. With forming gas as the reactive gas atmosphere,

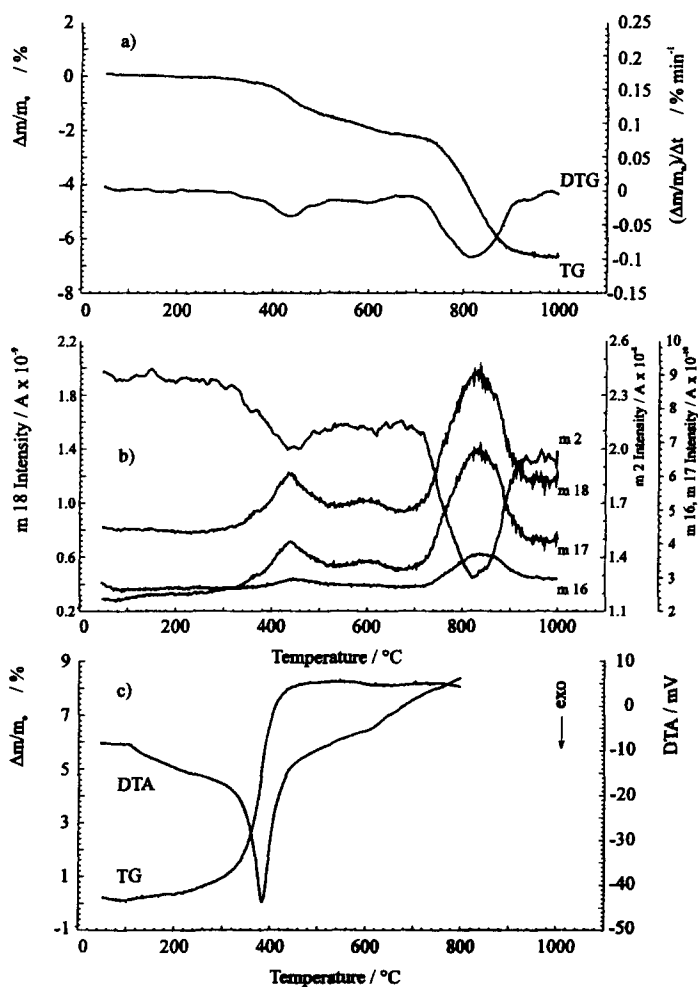


Fig. 5. Thermal behaviour of $\text{YBaCoCu}_{0.4}\text{Fe}_{0.6}\text{O}_{5+\delta}$: (a) TG and DTG under 5% H_2/N_2 ; (b) simultaneously monitoring MS with $m\ 2$ for H_2 , $m\ 18$, $m\ 17$, $m\ 16$ for H_2O , HO^+ and O^{2+} ; (c) reoxidation of the reduced product with O_2 as observed by TG and DTA.

a stepwise degradation of the sample was observed by TG – DTG as well as by coupled MS monitoring of the composition of the carrier gas ($m\ 2$) and the volatile products of reduction originating from H_2O . The reduction takes place in three steps and is accompanied by a mass loss of 1.4% between 300 and 500°C, 0.8% between 500 and 740°C, and 4.3% in the range 740–950°C. XRD of the product reveals a complete decomposition of the initial structure. In analogy to the prior sample, the TG – DTG changes correspond exactly to the peaks determined by MS for the formation of H_2O and the simultaneous decrease of hydrogen in the carrier gas. While the overall mass loss of 6.5% is in agreement with the prior sample, the course of reduction is different.

The higher iron content seems to have a stabilizing effect, shifting the reductive step with the main loss of oxygen to higher temperatures.

Again, the product of reduction is reoxidized in a strong exothermic reaction under pure oxygen as shown in Fig. 5c. According to XRD, a perovskite phase is reformed. As the oxygen uptake of 8.5% is distinctively higher than the sum of losses during reduction, additional oxygen might have been incorporated into the lattice due to a complete oxidation of Fe and Co into the trivalent state.

From the literature describing the parent compounds, the valences were determined as Fe(III) according to Mössbauer spectroscopy, and as Cu(II), and a mixed valent system of Co(II)/Co(III) from XANES [3, 6, 7]. The methods applied in this study did not allow the oxidation states of the different redox-active cations to be distinguished. Therefore, changes in the overall oxidation states were formally attributed to the cobalt ions, while others were assumed as Fe(III) and Cu(II).

Investigation of the as-prepared powders under pure oxygen atmosphere revealed that no oxidation was possible for $\text{YBaCuFe}_{0.4}\text{Co}_{0.6}\text{O}_{5+\delta}$, thus pointing to an oxidation state of Co(III) in this sample. However, for the sample of composition $\text{YBaFeCu}_{0.4}\text{Co}_{0.6}\text{O}_{5+\delta}$ from the first group of materials, a mass gain of 0.2% was observed corresponding to an uptake of 0.05 oxygen per mol of the sample or an oxidation of 0.1 mol Co(II) into the trivalent state.

The third group of materials was systematically investigated with respect to its thermodynamic behaviour in pure oxygen atmosphere. Starting from the composition YBaCoCuO_5 with Co in the trivalent state [8], a partial substitution of Cu(II) by Fe(III) presents two possible evolutions of the system. Firstly, with increasing amounts of Fe(III) cobalt might be simultaneously reduced to Co(II) leading to an overall oxygen content of O_5 . Secondly, additional oxygen might be incorporated into the vacancies of the oxygen-deficient structure by increasing the Fe(III) content.

The experiments were performed for the samples $\text{YBaCoCu}_{1-x}\text{Fe}_x\text{O}_{5+\delta}$ with $x = 0.4, 0.6$ and 0.8 , as illustrated in Fig. 6. All powders revealed an uptake of oxygen starting from 260°C and reaching a maximum at about 400°C. For a further increase of the temperature, a reversible release of oxygen from the lattice was established. All samples showed a slow, linear mass loss between 400 and 700°C, basically returning to their original values prior to annealing.

No DTA peaks were observed in this range. This leads to the assumption that above 400°C, i.e. when the oxide ions gain mobility to diffuse through the lattice, the systems return to their original valences and oxygen content, apparently thermodynamically more stable in this range. For $\text{YBaCoCu}_{0.4}\text{Fe}_{0.6}\text{O}_{5+\delta}$ and $\text{YBaCoCu}_{0.2}\text{Fe}_{0.8}\text{O}_{5+\delta}$ above 700°C, another oxidation process is observed due to a mass gain of 0.1%.

The amount of oxygen uptake up to the maximum at about 400°C increases linearly with increasing partial substitution of Cu through Fe. Assuming, see Ref. [7], that the perovskite B-cations are incorporated as Fe(III), Cu(II) and Co(II)/Co(III), the observed effects can be explained in a way such that with increasing substitution of Fe(III) the amount of cobalt ions incorporated as Co(II) rises simultaneously. These Co(II) cations are subject to oxidation at 260–400°C to Co(III), followed by the incorporation of additional oxygen into the vacancies of the two-dimensional structure. In this sense, the mass gain of 0.1% of $\text{YBaCoCu}_{0.6}\text{Fe}_{0.4}\text{O}_{5+\delta}$ (presumably $\text{YBaCo(III)}_{0.6}\text{Fe(III)}_{0.4}$

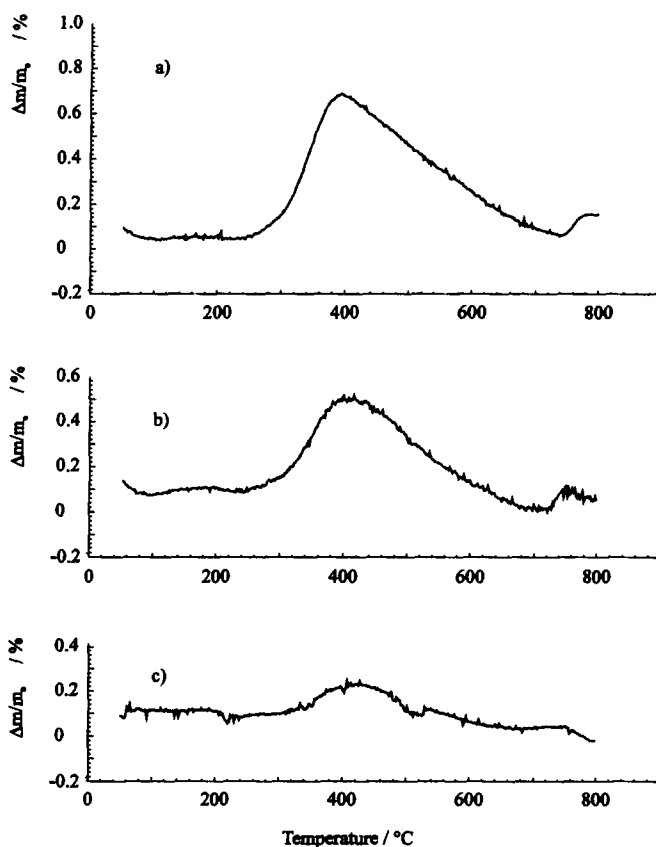


Fig. 6. Thermogravimetric measurements in pure oxygen atmosphere for: (a) $\text{YBaCoCu}_{0.2}\text{Fe}_{0.8}\text{O}_{5+\delta}$; (b) $\text{YBaCoCu}_{0.4}\text{Fe}_{0.6}\text{O}_{5+\delta}$; and (c) $\text{YBaCoCu}_{0.6}\text{Fe}_{0.4}\text{O}_{5+\delta}$.

$\text{Cu(II)}_{0.6}\text{Co(II)}_{0.4}\text{O}_{5+\delta}$) corresponds to an oxygen uptake of 0.43 g or $\text{O}_{0.03}$ per mol sample, or an oxidation of 0.05 Co(II) to Co(III) respectively. This effect is more pronounced for the samples with higher Fe content: $\text{YBaCoCu}_{0.4}\text{Fe}_{0.6}\text{O}_{5+\delta}$ ($\text{YBaCo(III)}_{0.4}\text{Fe(III)}_{0.6}\text{Cu(II)}_{0.4}\text{Co(II)}_{0.6}\text{O}_{5+\delta}$) shows a mass gain of 0.4% corresponding to an increase in the oxygen content by 1.70 g or $\text{O}_{0.10}$ per mol substrate and equivalent to an oxidation of 0.21 mol $\text{Co(II)} \rightarrow \text{Co(III)}$. The increase in mass of 0.7% for $\text{YBaCoCu}_{0.2}\text{Fe}_{0.8}\text{O}_{5+\delta}$ ($\text{YBaCo(III)}_{0.2}\text{Fe(III)}_{0.8}\text{Cu(II)}_{0.2}\text{Co(II)}_{0.8}\text{O}_{5+\delta}$) corresponds to an oxygen gain of 2.96 g or $\text{O}_{0.19}$ per mol of the sample due to the oxidation of 0.37 mol Co(II).

According to these results the incorporation of oxygen into the vacancies is limited to a certain amount as the Co cations are not completely oxidized to the trivalent state, thus basically conserving the layered structure as the main structural element.

If there is a reversible incorporation and release of oxygen into this perovskite-related structure, an additional uptake of oxygen into the lattice should be observed by

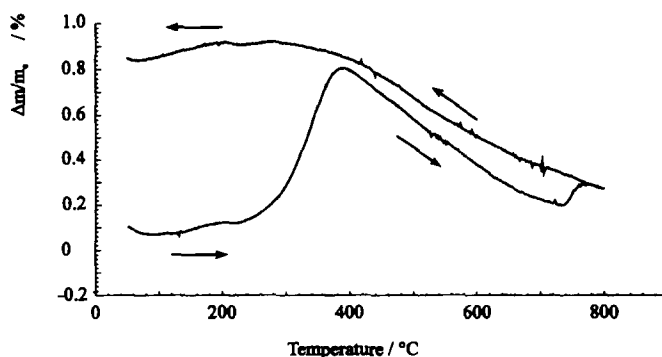


Fig. 7. Thermogravimetric measurements for $\text{YBaCoCu}_{0.2}\text{Fe}_{0.8}\text{O}_{5+\delta}$ by reversibly cycling to 800°C and back to room temperature in pure oxygen atmosphere.

cooling the sample in pure oxygen atmosphere from 800 back to 400°C. During a further cooling process to room temperature, the oxygen should remain in the lattice as the diffusion is limited within this temperature range. This experiment was performed with $\text{YBaCoCu}_{0.2}\text{Fe}_{0.8}\text{O}_{5+\delta}$ as demonstrated in Fig. 7, and was in complete agreement with the prediction. Therefore, the reversible incorporation of oxygen by the redox-active metal cations in mixed valences could be confirmed.

With these results, the design of new catalytic systems may be achieved. For example, Co catalysts are used for the production of long-chain hydrocarbons from synthesis gas (Fischer–Tropsch) [9]. One specific feature of these catalysts is the partial reduction with CO/H_2 to cobalt oxides of different valences and Co metal. A heterovalent Co system can be achieved in this substituted perovskite-related phase by different approaches. On the one hand, the oxidation states of the incorporated Co cations may be controlled by the composition of the samples, i.e. by the extent of partial substitution and by the specific cations replaced by Co. On the other, different gas atmospheres influence the valency and oxygen content of the samples, be it in flowing oxygen leading to a reversible incorporation of oxygen as already demonstrated in Fig. 7, or in reducing conditions forming partially or completely reduced systems including Co metal as identified in the XRD pattern of the products in Fig. 4b–d. Moreover, the formation of new ternary compounds in the progress of metal-selective reduction of Co and Cu may act as supporting promoters of the Co catalyst to enhance the selectivity of the chemical reaction. The catalytic activities of these samples have to be pursued in future investigations.

4. Conclusions

In conclusion, the studied samples of the three different substituted groups of materials exhibited different behaviour during thermal treatments. For the system $\text{YBaFe}_{1-x}\text{Co}_x\text{CuO}_{5+\delta}$ studied for $x = 0.6$, no further oxidation was possible by annealing in pure oxygen, indicating that Co is indeed incorporated as Co(III). In

contrast, for the two groups of materials $\text{YBaFeCu}_{1-x}\text{Co}_x\text{O}_{5+\delta}$ (studied for $x = 0.6$) and $\text{YBaCoCu}_{1-x}\text{Fe}_x\text{O}_{5+\delta}$ (with $x = 0.4, 0.6$ and 0.8), an oxidation was observed by an increase in mass due to the incorporation of additional oxygen, probably into the vacancies of the oxygen-deficient layered structure. The mass gain registered by thermogravimetry with increasing partial substitution is consistent with the results from the literature that the B-cations in this structure are present as Cu(II), Fe(III) and a mixed valency of Co(II)/Co(III). The existence of a redox-active heterovalent system could be proved by a reversible cycling of TG with $\text{YBaCoCu}_{0.2}\text{Fe}_{0.8}\text{O}_{5+\delta}$ in O_2 between room temperature and 800°C .

These heterovalent materials may act as possible catalysts for partial oxidation processes, be it in oxidizing atmosphere with an active mixed valency of Co(II)/Co(III), or under reducing conditions combined with a metal-selective reduction of Co to create an active species for adsorption. The reactivity and selectivity of these materials might possibly be controlled by different ratios of substitution; further investigations are necessary for verification of this, however.

Acknowledgements

The author wishes to thank Prof. Dr. A. Reller and Prof. Dr. W. Dannecker, Institute of Inorganic and Applied Chemistry, University of Hamburg, for use of their equipment and for valuable discussions. Additionally financial support by the Fonds der Chemischen Industrie is very much appreciated.

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