

REVERSIBLE CYCLING OF THE OXYGEN CONTENT IN Co-SUBSTITUTED $\text{YBaFeCuO}_{5+\delta}$

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Abstract

The reversible cycling of the oxygen content in layered Co-substituted perovskites of type $\text{YBaFeCuO}_{5+\delta}$ was investigated applying thermoanalytical methods. For the system $\text{YBaCoCu}_{1-x}\text{Fe}_x\text{O}_{5+\delta}$ an increasing amount of oxygen incorporation into the oxygen deficient lattice was found by thermogravimetry for an increasing iron content of $x = 0.4$ to 0.8 . With a cycle of subsequent heating and cooling the reversible incorporation of oxygen on account of redox active cations with mixed valencies could be demonstrated. The combination of several cycles under different gas atmospheres confirmed the reversibility of the oxidation processes suggesting the application for catalytical processes.

Keywords: perovskite, reversible oxygen incorporation, thermal reactivity, thermogravimetry

Introduction

The perovskite of chemical composition $\text{YBaFeCuO}_{5+\delta}$ adopts a layered structure with defined oxygen vacancies. This ordered oxygen deficient twodimensional structure 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, as demonstrated in Fig. 1. A possible ordering of CuO_5 and FeO_5 pyramids is discussed in the literature [1, 2].

The perovskite B-cations Cu or Fe were successfully partially substituted by Co leading to pure ceramic materials according to powder X-ray diffraction [3].

Under the influence of various gas atmospheres during thermal analysis different oxidation states of the cations in the B-position can be achieved, including mixed valencies. Reducing conditions ($5\% \text{H}_2/\text{N}_2$) lead to metal selective reduction processes due to stabilizing effects of additional vacancies in the perovskite structure and/or a complete degradation of the structural framework. Both reactions can be reversed by topochemical processes [4].

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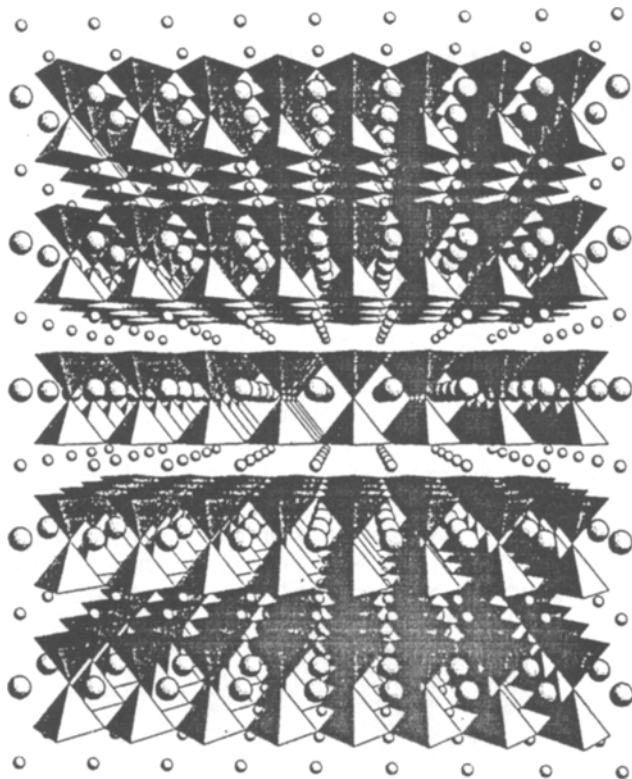


Fig. 1 Layered perovskite structure of YBaFeCuO_5 (Ba large circles, Y small circles, Fe/CuO₅ pyramids)

The scope of the present work is to study the thermochemical reversibility of these partial redox processes accompanied by the incorporation and release of oxygen from the lattice. The reversible cycling of annealing and cooling in oxidative and inert gas atmosphere is monitored by thermogravimetry in order to investigate the incorporation of oxygen into the vacancies for samples with different Fe/Cu/Co ratios. The reversibility of these partial oxidation processes is observed with respect to a variation of the temperature as well as to a combination of several temperature cycles in different gas atmospheres.

Redox catalyzed partial oxidation reactions, e.g. the conversion of nitrogen oxides resulting from combustion engines, might possibly be enhanced with respect to the chemical composition of these Co-substituted perovskites.

Experimental

Samples of nominal composition $\text{YBaFeCu}_{1-x}\text{Co}_x\text{O}_{5+\delta}$, $\text{YBaFe}_{1-x}\text{Co}_x\text{CuO}_{5+\delta}$ 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 conventional solid state reaction and characterized as described in [3]. Thermoanalytical measurements were carried out with a Netzsch STA 409 coupled to a quadrupole mass spectrometer (Balzers QMG 421). The experiments were performed under different gas atmospheres of Argon, pure oxygen

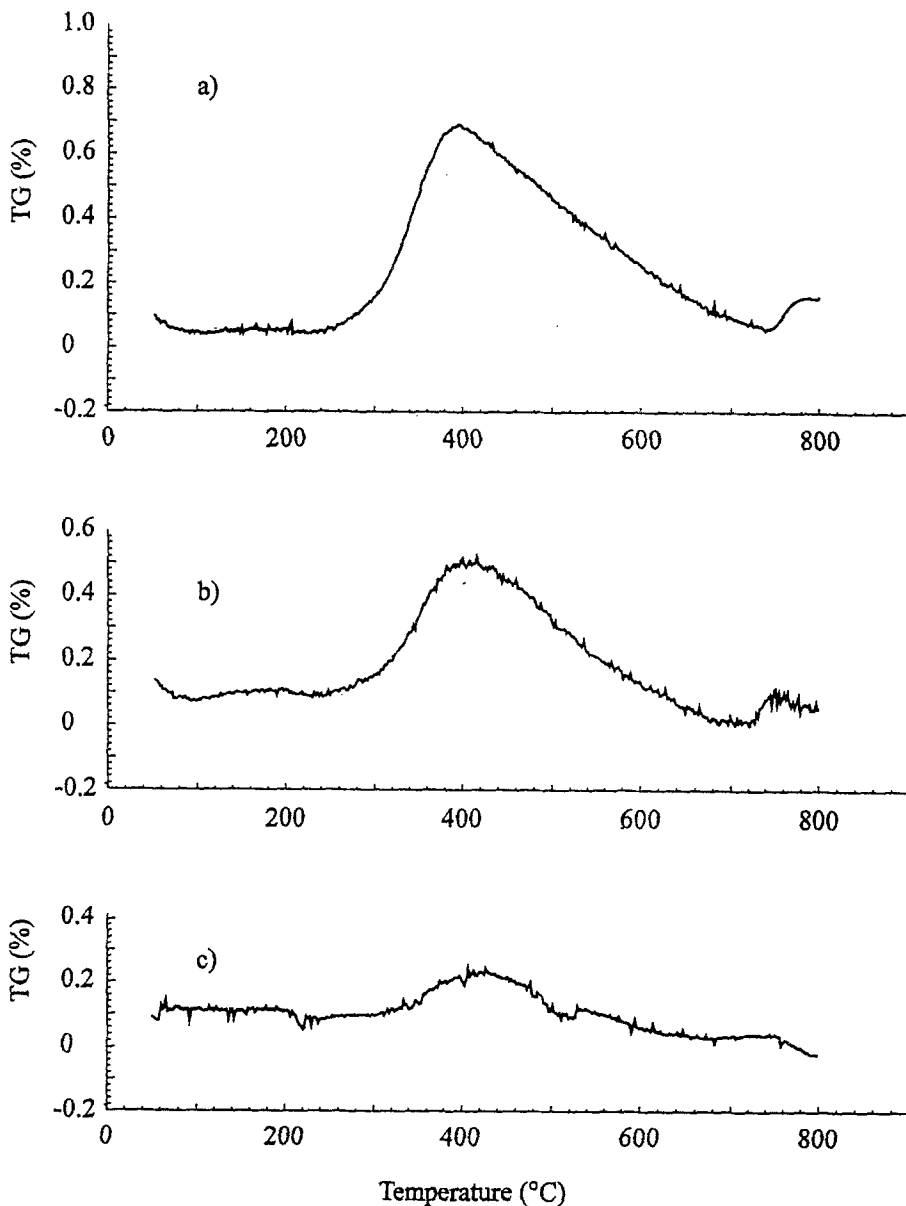


Fig. 2 Thermogravimetric measurements in pure oxygen atmosphere for a) $\text{YBaCoCu}_{0.2}\text{Fe}_{0.8}\text{O}_{5+\delta}$, b) $\text{YBaCoCu}_{0.4}\text{Fe}_{0.6}\text{O}_{5+\delta}$ and c) $\text{YBaCoCu}_{0.6}\text{Fe}_{0.4}\text{O}_{5+\delta}$

or of forming gas (5% H_2N_2) with a flow rate of 0.02 l min^{-1} . The temperature was raised up to 800°C using a heating rate of 5°C min^{-1} . All thermogravimetric curves were corrected for buoyancy.

Results and discussion

The group of powder materials $\text{YBaCoCu}_{1-x}\text{Fe}_x\text{O}_{5+\delta}$ with $x=0.4, 0.6$ and 0.8 was systematically investigated with respect to its thermochemical behaviour in pure oxygen atmosphere. The resulting curves of thermogravimetry are illustrated in Fig. 2. 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 continuous release of oxygen from the lattice was established. All samples showed a slow and linear weight loss between 400 and 700°C basically returning to their original values prior to annealing. No peaks of DTA were observed in this range.

The amount of oxygen uptake up to the maximum at about 400°C increases linearly with increasing partial substitution of Cu through Fe. With the assumption referring to the literature [5] 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 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 $260\text{--}400^\circ\text{C}$ to Co(III) followed by the incorporation of additional oxygen into vacancies of the twodimensional structure.

Accordingly 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 [4].

A reversible cycle of heating and subsequent cooling in pure oxygen is shown in Fig. 3 for $\text{YBaCoCu}_{0.2}\text{Fe}_{0.8}\text{O}_{5+\delta}$. The additional cooling process lead to a reversible uptake of oxygen between 800 and 400°C followed by a basically constant weight for further cooling to room temperature due to the limited mobility of oxygen in the lattice for lower temperatures. Thus the reversible incorporation of oxygen with respect to the redox active cations in mixed valencies could be confirmed including the possibility to realize higher oxidized products by the cooling process in O_2 .

The reversibility of the thermochemical redox processes gives rise to investigate a combination of several thermal cycles under different conditions. Fig. 4 illustrates the temperature dependent curves of thermogravimetry of $\text{YBaCoCu}_{0.2}\text{Fe}_{0.8}\text{O}_{5+\delta}$ for a temperature program of four subsequent cycles. During cycle 1 the sample was heated to 800°C and cooled in O_2 . Then the carrier gas was changed to Argon in cycle 2 with the same temperature procedure. Cycle 3 and 4 were again performed under pure oxygen up to a maximum temperature of 800 and 400°C respectively. The results can be summarized as follows:

The maximum weight due to oxygen incorporation under O_2 atmosphere is observed at 400°C passing through the heating as well as the cooling program.

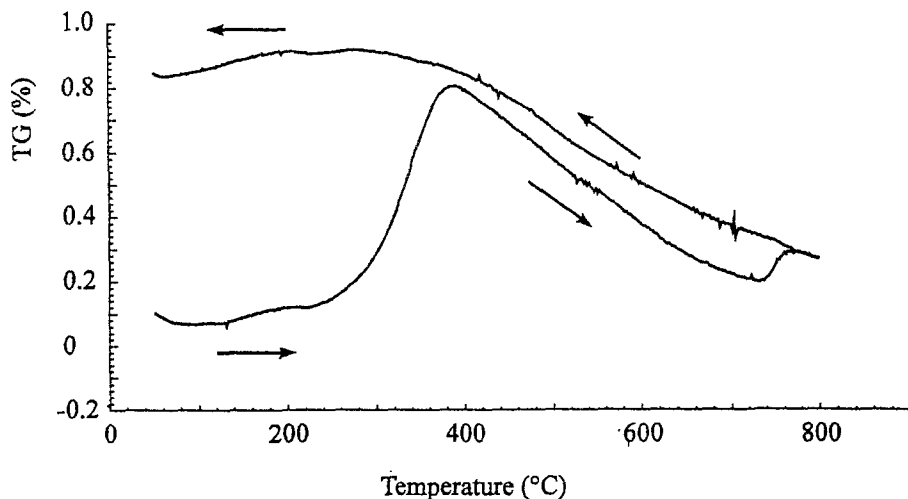


Fig. 3 Thermogravimetric measurements for $\text{YBaCoCu}_{0.2}\text{Fe}_{0.8}\text{O}_{5+\delta}$ by reversibly cycling to 800°C and back to room temperature in pure oxygen atmosphere

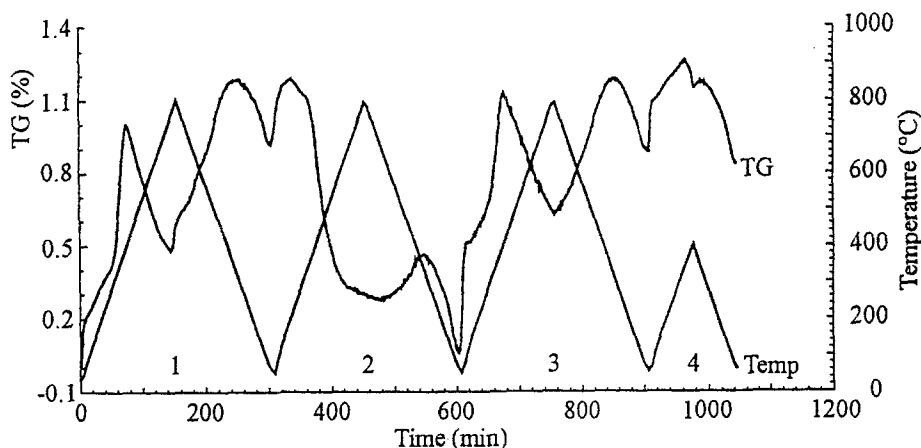


Fig. 4 Thermogravimetry of $\text{YBaCoCu}_{0.2}\text{Fe}_{0.8}\text{O}_{5+\delta}$ for a temperature program of four subsequent heating and cooling cycles: cycle 1, 3 and 4 in O_2 , cycle 2 in Ar atmosphere

The values of the maxima are slightly higher during the cooling procedure leading to higher oxygen contents compared to the corresponding heating segment. Two subsequent cycles in oxygen atmosphere do not give rise to a further step-wise enrichment of the oxygen content. The conversion to Argon as carrier gas for the second thermal cycle induced a release of oxygen upon heating at 360°C and reached the originating weight or oxygen content respectively prior to the experiment. A reset to pure oxygen atmosphere for the cycles 3 and 4 was followed by a reversible re-incorporation of oxygen exhibiting an identical behav-

our during thermogravimetry as in cycle 1. Setting the maximum temperature for the reverse from the heating to the cooling process on the point of maximum oxygen uptake (400°C) does not lead to a distinct increase of the final oxygen content.

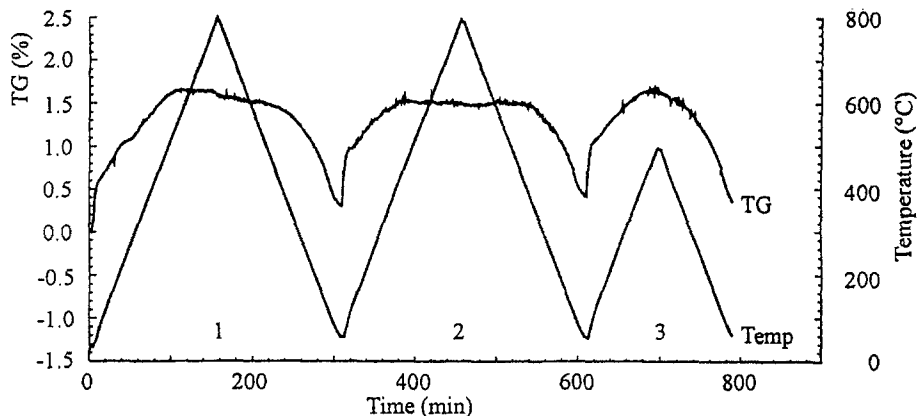


Fig. 5 Thermogravimetry of $\text{YBaFeCu}_{0.4}\text{Co}_{0.6}\text{O}_{5+\delta}$ for three cycles in O_2

A comparable treatment was performed with $\text{YBaFeCu}_{0.4}\text{Co}_{0.6}\text{O}_{5+\delta}$ for three cycles in pure oxygen as shown in Fig. 5. As for the previous sample a reversible incorporation was found. However, no increase of the overall oxygen content could be achieved on the performance of several subsequent cycles nor for the reverse of the treatment at the temperature of maximum weight gain (500°C). In contrast to the previous powder this sample showed only a minor effect of oxygen release after passing through the maximum value at 500°C . However the overall effect of redox activity was also less pronounced.

Conclusions

For distinct samples of the Co-substituted perovskites of type $\text{YBaFeCuO}_{5+\delta}$ the thermochemical reactivity was observed by thermoanalytical methods. The existence of a redox active heterovalent system could be proved with thermogravimetry by a reversible cycling of the oxygen content in O_2 between room temperature and 800°C . The highest activity could be established for the powder of chemical composition $\text{YBaCoCu}_{0.2}\text{Fe}_{0.8}\text{O}_{5+\delta}$. A combination of several thermal treatments in different gas atmospheres confirmed the reversible redox processes. These heterovalent materials may act as possible catalysts for partial oxidation processes in oxidizing atmosphere with an active mixed valency of Co(II)/Co(III) .

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