Magnetization, Mössbauer and isothermal dilatometric behavior of oxidized 

\[ \text{YBa(}\text{Co,Fe)}_{4}\text{O}_{7+\delta} \]

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Abstract

Mössbauer spectroscopy and magnetization studies of YBaCo_{4-x}Fe_{x}O_{7+\delta} (x = 0-0.8) oxidized at 0.21 and 100 atm O_{2}, indicate an increasing role of penta-coordinated Co^{3+} states when the oxygen content approaches 8-8.5 atoms per formula unit. Strong magnetic correlations are observed in YBaCo_{4-x}Fe_{x}O_{8.5} from 2 K up to 55-70 K, whilst the average magnetic moment of Co^{3+} is lower than that for \( \delta \leq 0.2 \), in correlation with the lower \( ^{57}\text{Fe}^{3+} \) isomer shifts determined from Mössbauer spectra. The hypothesis on dominant 5-fold coordination of cobalt cations was validated by molecular dynamics modeling of YBaCo_{4}O_{8.5}. The iron solubility limit in YBaCo_{4-x}Fe_{x}O_{7+\delta} corresponds to approximately x \( \approx 0.7 \). The oxygen intercalation processes in YBaCo_{4}O_{7+\delta} at 470-700 K, analyzed by X-ray diffraction, thermogravimetry and controlled-atmosphere dilatometry, lead to unusual volume expansion opposing to the cobalt cation radius variations. This behavior is associated with increasing cobalt coordination numbers and with rising local distortions and disorder in the crystal lattice on oxidation, predicted by the computer simulations. When the oxygen partial pressure increases from 4\times10^{-5} to 1 atm, the linear strain in YBaCo_{4}O_{7+\delta} ceramics at 598 K is as high as 0.33\%.
1. Introduction

YBa$_2$Co$_4$O$_{7+\delta}$-based phases and their derivatives attract a significant attention due to their potential applications for oxygen sorption and electrode materials, and to very unusual structural and magnetic behavior.$^{1-15}$ The crystal lattice of YBa$_2$Co$_4$O$_7$ and its analogues consists of closely packed alternating triangular and Kagomé-type layers of corner sharing CoO$_4$ and Co$_2$O$_4$ tetrahedra, respectively, leading to strongly frustrated spin systems. The structure symmetry and magnetic properties of YBa$_2$Co$_4$O$_{7+\delta}$-type compounds appear very sensitive to oxygen content and even to the materials morphology, which often causes disagreements in the literature. The YBa$_2$Co$_4$O$_7$ structure has initially been described as hexagonal (space group $P6_{3}mc$).$^5$ According to Refs.$^6-8$, only the samples annealed in an inert atmosphere like flowing N$_2$ contain exactly 7 oxygen anions per formula unit (f.u.) and display long-range magnetic ordering. A neutron diffraction study of such an oxygen-stoichiometric material showed that the high-temperature paramagnetic trigonal structure (S.G. $P31c$) transforms at $T_S = 313$ K into orthorhombic $Pbn2_1$, relieving the geometric frustration in YBa$_2$Co$_4$O$_7$ and giving rise below 110 K to an extended regime of short-range correlations followed by 3D antiferromagnetic (AF) ordering.$^6$ More recently, single-crystal neutron diffraction and high-resolution X-ray powder diffraction (XRPD) analyses demonstrated that the long-range magnetic ordering in YBa$_2$Co$_4$O$_7$ is associated with a structural transition from orthorhombic $Pbn2_1$ to monoclinic $P11_2_1$ symmetry at 100 K,$^1$ a monoclinic distortion at lower temperatures was also reported in Ref.$^6$. YBa$_2$Co$_4$O$_{7+\delta}$ synthesized in air above 1223-1273 K and quenched, is often oxygen-hyperstoichiometric$^6$-$^9$ and still exhibits strong AF interactions and negative Curie-Weiss temperature ($\Theta_{CW}$), but shows glassy behavior with a freezing temperature $T_{MF} = 66$ K.$^{10}$ Huq et al.$^8$ reported that the YbBa$_2$Co$_4$O$_{7.2}$ sample was biphasic and the oxygen-rich component remained in the $P31c$ symmetry down to 10 K which probably inhibits the 3D AF ordering. In a single crystal the presence of diffuse magnetic scattering at low temperatures was identified, suggesting short-range magnetic correlations in both triangular and Kagomé layers.$^{11}$

In the low-temperature range YBa$_2$Co$_4$O$_{7+\delta}$-based compounds are thermodynamically metastable, but can absorb large amounts of oxygen without phase decomposition at least up to 870 K.$^2$ Annealing YBa$_2$Co$_4$O$_{7+\delta}$ at 520-630 K in air or O$_2$ or using other oxygenation approaches rises the oxygen content up to 8.0-8.56 ions/f.u.,$^{2,7}$ although the values above 8.5 may relate to the surface sorption or even be a sign of starting phase separation that becomes extensive at temperatures above 970-1070 K in air. While the XRD patterns of YBa$_2$Co$_4$O$_{7+\delta}$ with $\delta < 1$ can be refined in the $P6_{3}mc$ or $P31c$ space groups, the structure of YBa$_2$Co$_4$O$_{8.1}$ (so-called “O8”) was described as $Pbc2_1$.$^{12}$ No structural transition or long-range AF ordering in YBa$_2$Co$_4$O$_{8.1}$ was observed down to 10 K.$^{12}$ Mössbauer spectroscopy (MS) of $^{57}$Fe-doped YBa$_2$Co$_4$O$_{7+\delta}$ ($\delta = 0.02$ and 0.8) showed that gradual freezing of the iron magnetic moments occurs below $T_{MF}$ temperature in an inverse correlation with the extra oxygen content.$^{13}$
To authors’ knowledge, the crystal structure of YBaCo$_4$O$_{8.5}$ has not been determined as yet, though detailed structural investigations are in progress.$^8,^{14}$ Note also that transmission-electron microscopy (TEM) revealed different types of superstructure within the same powder grains of YBaCo$_4$O$_{8.5}$, suggesting that the excess oxygen anions appear incorporated in the YBaCo$_2$O$_7$ parent lattice in different configurations.$^{15}$ The possibility to partially replace Co by Fe in YBaCo$_4$O$_{7+\delta}$ which may enable to modify oxygen sorption properties and anion diffusivity important for the practical applications, was already reported in the literature. In particular, polycrystalline YBaCo$_{1.2}$Fe$_{0.8}$O$_{7+\delta}$ $^{16,17}$ and single-crystal YBaCo$_3$FeO$_7$ $^{18}$ isostructural to YBaCo$_2$O$_7$ were obtained. No information on the iron solubility limits in YBaCo$_4$O$_{7+\delta}$ ($\delta = 0-1.5$) is however available.

The present work is centered on the magnetization measurements, evaluation of chemically-induced lattice strains, computer modeling of the oxygen intercalation processes using the molecular dynamics (MD) and static-lattice simulation (SLS) approaches, and $^{57}$Fe Mössbauer spectroscopy of YBaCo$_{4-x}$Fe$_x$O$_{7+\delta}$ ($x = 0-0.8$, $0.02 \leq \delta \leq 1.5$). The isothermal chemical expansion induced by the redox processes in YBaCo$_2$O$_{7+\delta}$, which is a key factor determining materials applicability for the ceramic membranes and electrodes, was studied by the controlled-atmosphere dilatometry. For MS studies, a probe of 1% $^{57}$Fe isotope was introduced in YBaCo$_2$O$_{7+\delta}$ in order to assess local structural features and magnetic interactions. The Mössbauer spectra of YBaCo$_{3.96}$ $^{57}$Fe$_{0.04}$O$_{7+\delta}$ ($\delta = 0.02$ and 0.8) have already been reported elsewhere$^{13}$ and are only used in this work for the sake of comparison.

2. Experimental

Polycrystalline powders of YBaCo$_{4+\delta}$, YBaCo$_{3.96}$ $^{57}$Fe$_{0.04}$O$_{7+\delta}$ and YBaCo$_{3.2}$Fe$_{0.8}$O$_{7+\delta}$ were synthesized via glycine-nitrate process followed by annealing in air at 1273-1473 K for 20 h with intermediate regrindings, as described in previous work.$^{13}$ In the case of $^{57}$Fe-rich YBaCo$_{3.96}$Fe$_{0.04}$O$_{7+\delta}$, the stoichiometric amount of metallic iron enriched with $^{57}$Fe isotope (chemical purity 99.96%, $^{57}$Fe content 95.73%, Chemgas, France) was dissolved in diluted nitric acid and then added in an aqueous glycine-nitrate solution containing the metal cations in calculated proportions. For YBaCo$_{3.2}$Fe$_{0.8}$O$_{7+\delta}$, high-purity Fe$_2$O$_3$·2H$_2$O with natural iron was dissolved in a nitric acid solution and used for the synthesis. All other starting materials and experimental conditions were identical. Dense ceramic disks were compacted at 120-180 MPa, sintered in air at 1473-1523 K, and then either cut into bars ($4\times4\times15$ mm$^3$) for dilatometric measurements or ground into powders for other analyses. In order to prepare materials where the total oxygen content (7+$\delta$) is close to 7, 8 and 8.5 atoms/f.u. (Table 1), different series of the samples were rapidly cooled after annealing in air at 1303-1473 K for 5-22 h, in air at 598 K for 18 h, and under the oxygen pressure of 100 atm at 598 K for 15 h, respectively.
Room-temperature XRPD patterns were collected using PANalytical X’Pert Pro and Rigaku D/MAx-B diffractometers (CuKα, 2θ = 10-100°, step 0.015-0.020°, 3-15 s/step). All the samples were found single-phase, except for YBaCo_{3.2}Fe_{0.8}O_{7+δ} where the XRPD patterns display a small (~3%) extra peak attributed to the secondary perovskite-like phase as discussed below, Fig.1. Notice also that for the samples oxidized at 598 K in air and under 100 atm O_2, the superstructure reflections are clearly visible in the patterns, in agreement with literature.\textsuperscript{8,12,14}

The values of oxygen content, 7+δ, listed in Table 1, were determined by thermogravimetric analysis (TGA, Setaram SetSys 16/18 instrument). Fig.2 presents two examples of the TGA curves collected on heating in air and subsequent total reduction of in flowing dry 10% H_2 - 90% N_2 gas mixture at 1273-1423 K. The first measuring regime with isothermal dwells at 598-773 K (Fig.2A) was used to optimize the oxidation temperature and time, ensuring incorporation of a definite amount of oxygen in metastable YBa(Co,Fe)O_{7+δ} without phase decomposition. The second regime (Fig.2B) was used to study oxygen sorption on continuous heating in air. Both regimes were used in parallel with high-temperature XRPD analysis in order to evaluate any structural changes accompanying the oxygen uptake and desorption processes. The final reduction in 10% H_2 - 90% N_2, when the stoichiometric mixtures of binary metal oxides and metallic Co and Fe were formed, made it possible to calculated the absolute values of the oxygen content.

High-temperature XRPD data were collected using a PANalytical X’Pert Pro diffractometer equipped with an Anton Paar HTK-2000 heating stage at 298-1373 K. The controlled-atmosphere dilatometric studies of YBaCoO_{7+δ} ceramics were carried out using a Linseis L75V/1250 instrument, as described elsewhere.\textsuperscript{19} The tests were performed on heating in air up to 598 K and then in the isothermal regime, switching the atmosphere between flowing air, O_2 and Ar where the oxygen partial pressures (p(O_2)) are equal to 0.21, 1.0 and 4×10^{-5} atm, respectively.

The Mössbauer spectra were collected at 4-295 K in transmission mode using a conventional constant-acceleration spectrometer and a 25 mCi \(^{57}\)Co source in a Rh matrix. The absorbers were obtained by pressing the powdered samples into perspex holders; the velocity scale was calibrated using α-Fe foil. The room-temperature spectra were obtained under vacuum (~10^{-3} atm). At low temperatures a JANIS bath cryostat (model SVT-400) was used. The spectra were fitted to Lorentzian lines; when necessary distributions of magnetic splittings were analyzed according to the histogram method. Magnetization was measured on free powder samples using a S700X SQUID instrument (Cryogenic Ltd., UK). For all the samples, the magnetization under different fields was determined on heating from 2 up to 300 K, after cooling the samples from the highest temperature in zero field (zero-field-cooled, ZFC) or in the measurement field (field-cooled, FC).

Description of the computer simulation methods employed in this work, specific procedures and software (DL POLY 2 for MD and GULP for SLS), is found in Refs.\textsuperscript{20-24}. The interatomic potentials were taken from \textsuperscript{25-28};
the initial supercells used for modeling were built using the structural data on YBaCo$_4$O$_7$ and YBaCo$_4$O$_{8.5}$.

In order to form YBaCo$_4$O$_{8.5}$ supercell where all cobalt cations are trivalent, extra anions were placed in four equivalent positions $\{0.37, 0.56, 0.69\}$, $\{0.69, 0.44, 0.18\}$, $\{0.63, 0.06, 0.69\}$ and $\{0.37, 0.94, 0.18\}$ available for possible oxygen intercalation in the YBaCo$_4$O$_8$ lattice, with simultaneous increase of the cobalt oxidation state. Note that these four positions originate from multiplication of a single site in the primitive cell by lattice symmetry. If using the primitive cell with pre-defined symmetry, possibilities of the GULP structure optimization become limited. To avoid this limitation, all the SLS operations were performed on the entire supercell with the symmetry reduced to P1. The supercells consisting of 4×5×5 unit cells (~11600 atoms) were built and relaxed using GULP software, and then transferred to DL_POLY for MD simulations. In the course of MD studies, the lattices were initially equilibrated at $T_{\text{MD}} > 1400$ K in the $\text{npt hoover thermostat}$ regime for volume relaxation and anions redistribution in the vicinity of their equilibrium positions. Then the supercells were consecutively cooled down, with 100-200 K steps and complete equilibration at each temperature (100-500 ps). Final data were collected in the $\text{nve}$ thermostat regime for at least 100000 MD steps. The results (atomic trajectories) were imported into SQLite database, which made it possible to analyze specific behavior of the lattice components considering individual atoms. For the analysis of cobalt environments, the atomic positions were averaged for 100000 steps (100 ps).

3. Results and discussion

3.1 Selected phase relationships at atmospheric oxygen pressure: an overview

Figure 3A presents an illustration of the YBaCo$_4$O$_{7+\delta}$ phase evolution on cooling in air, when oxidative decomposition starts at approximately 1173 K. The XRPD patterns were collected from 1373 K down to 873 K, with isothermal dwells after each 50 K in order to ensure that equilibration is achieved. No phase changes with time were observed above 1200 K. At 1173 K the decomposition products include Co$_3$O$_4$ and, most likely, perovskite-like solid solutions based on cubic BaCoO$_{3-\delta}$ (S.G. Pm$_3$m) and orthorhombic YCoO$_{3-\delta}$ (Pnma). The results agree well with the report showing that the formation of YBaCo$_4$O$_{7+\delta}$ phase can be achieved at 1173 K. For further evaluation of the stability limits and chemical strains due to oxidation at atmospheric oxygen pressure (see Fig.2), XRPD patterns were collected on temperature cycling between 298 and 773 K and between 473 and 1373 K, with another single-phase YBaCo$_4$O$_7$ sample preliminarily annealed in air at 1473 K for 22 h. The ratio of the refined unit cell parameters ($c/a$) is shown in Fig.4; Fig.3B illustrates phase changes observed on heating up to 1373 K. Irrespective of the oxidative decomposition processes that become clearly visible above 1000 K, at 473-693 K the temperature dependence of $c/a$ ratio correlates with the oxygen uptake which occurs without perovskite phase separation (Figs.2 and 4). For as-prepared materials, this intermediate-temperature oxidation process appears slow and only partially reversible. The isothermal XRPD scans at 573 K (Fig.5) show also that the $c/a$ ratio increases.
when oxygen is intercalated in the YBaCo$_{4}$O$_{7+\delta}$ lattice; the variations of the unit cell parameters are anisotropic, as for the layered nickelates. Taking into account the approximate phase stability regions marked by dashed lines in Fig.4, the oxidation of YBa(Co,Fe)$_{4}$O$_{7+\delta}$ at $0.21$ and $100$ atm O$_{2}$ for the Mössbauer and magnetic measurements was carried out at $598$ K. The same temperature was selected for the dilatometric tests. At higher temperatures, oxygen desorption from thermodynamically-metastable YBa(Co,Fe)$_{4}$O$_{7+\delta}$ starts to occur (Figs. 2 and 4); at temperatures below $570$-$580$ K the oxygen exchange kinetics is expected to further slow down.

3.2. Mössbauer spectra of YBaCo$_{3.96}$Fe$_{0.04}$O$_{7+\delta}$ and YBaCo$_{3.2}$Fe$_{0.8}$O$_{7+\delta}$ ($0 < \delta \leq 1.5$)

The analysis of Mössbauer spectra of $^{57}$Fe-enriched YBaCo$_{3.96}$Fe$_{0.04}$O$_{7+\delta}$ with $\delta = 0.02$-$0.80$ showed that all iron cations are trivalent. In the case of YBaCo$_{3.96}$ $^{57}$Fe$_{0.04}$O$_{7.02}$, at $4$ K two magnetic splittings are visible corresponding to tetrahedral sites in the Kagomé and triangular layers (Fig.6, Table 1). It should be emphasized that their fractions may not coincide with the crystallographic position ratio in YBaCo$_{4}$O$_{7}$ lattice since the relative site preferences of Fe$^{3+}$, Co$^{3+}$ and Co$^{2+}$ cations should be different. For YBaCo$_{3.96}$ $^{57}$Fe$_{0.04}$O$_{7.8}$ a third sextet is observed at $4$ K (Fig.6). Its isomer shift (IS) is higher than for the remaining two signals, suggesting the presence of Fe$^{3+}$ in higher coordination. The latter could correspond to the octahedral sites in the YBaCo$_{4}$O$_{8}$ structure proposed by Chmaissem et al. The difference in IS between the sites with higher and lower coordination is, however, small and may also be indicative of penta-coordinated Fe$^{3+}$. For YBaCo$_{3.96}$ $^{57}$Fe$_{0.04}$O$_{8.5}$ the peaks at $4$ K are broader than for the less oxidized samples. Distributions of magnetic hyperfine fields ($B_{hf}$) instead of single sextets are hence necessary to fit the spectrum, and at least three distributions are required. The average IS of all three components are slightly larger than those of tetra-coordinated Fe$^{3+}$ in YBaCo$_{3.96}$ $^{57}$Fe$_{0.04}$O$_{7.02}$. This difference reflects an increase in the average coordination numbers (CNs) but is very small again, characteristic rather of dominant 5-fold coordination.

On the other hand, the distributions may arise from the presence of different iron-oxygen polyhedra; the range of observed IS and $B_{hf}$ values corresponds to a diversity of possible near-neighbor configurations, making it impossible to resolve the sextets originating from 5- and 6-fold coordinated Fe$^{3+}$ with different local environments. Such a situation is consistent with that observed by selected area electron diffraction (SAED) and TEM in YBaCo$_{3.96}$O$_{8.5}$. The distributions with higher relative areas ($I$) in YBaCo$_{3.96}$ $^{57}$Fe$_{0.04}$O$_{8.5}$ spectrum mainly differ on their quadrupole shifts ($\epsilon$), whilst the IS and $B_{hf}$ values are close to each other, Table 1. The third distribution, with $I \approx 6\%$, exhibits significantly higher $B_{hf}$ and unusually large $\epsilon$ that may arise from heavy local distortions.

At room temperature, all the materials are paramagnetic (Fig.7). Although strong overlapping of the contributions hampers unique analysis of these spectra, it is still possible to check if a model consistent with the $4$ K data fits them adequately. Indeed, the room-temperature spectra can be described by several quadrupole doublets with relative areas similar to those of the $4$ K sextets, within the limits of experimental error (Table 1). The
corresponding IS are also consistent with those at 4 K, shifted to lower values by 0.10 - 0.13 mm/s as expected considering the second-order Doppler shift. The increase in the estimated quadrupole splittings (QS) with increasing oxygen content evidences larger distortions of the coordination polyhedra. As expected, iron cations in YBaCo$_{3.96}$Fe$_{0.04}$O$_{8.5}$ which give rise to a sextet with unusually high $\varepsilon$ at 4 K, also exhibit the highest QS at 295 K.

The temperature dependence of YBaCo$_{3.96}$Fe$_{0.04}$O$_{7.02}$ spectra indicates that the relaxation of all the Fe$^{3+}$ magnetic moments ($\mu_{\text{Fe}}$) slows down below ~10$^9$ Hz and becomes comparable to the corresponding Larmor-precession rate (order of magnitude 10$^7$ Hz) in the temperature range 70-75 K. The highest temperature where significant peak broadening is observed indicating that the $\mu_{\text{Fe}}$ relaxation drops below ~10$^9$ Hz, is $T_{\text{MF}} \approx 73$ K (Table 1). For YBaCo$_{3.96}$Fe$_{0.04}$O$_{7.8}$, this freezing starts at $T_{\text{MF}} \approx 70$ K but apparently only for the lower-coordinated Fe$^{3+}$ cations, while the remaining moments of Fe$^{3+}$ with higher CNs freeze below $T_{\text{MF}} \approx 55$ K. The latter situation is observed for all the Fe$^{3+}$ magnetic moments in YBaCo$_{3.96}$Fe$_{0.04}$O$_{8.5}$, again in correlation with the oxygen content.

One illustration of the Mössbauer spectra evolution with temperature, for YBaCo$_{3.96}$Fe$_{0.04}$O$_{8.5}$, is presented in ESI†. As for YBaCo$_{3.96}$Fe$_{0.04}$O$_{7+\delta}$, the MS analysis of YBaCo$_{3.2}$Fe$_{0.8}$O$_{7+\delta}$ demonstrates that the predominant oxidation state of iron is 3+ (Figs.8 and 9). This conclusion coincides with the results of X-ray absorption spectroscopy (XAS) studies of YBaCo$_3$FeO$_7$. Doping with iron increases the oxygen content in YBaCo$_{4-x}$Fe$_x$O$_{7+\delta}$; the $\delta$ values in YBaCo$_{3.2}$Fe$_{0.8}$O$_{7+\delta}$, measured by TGA, are approximately 0.2 at room temperature and 0.1 at 1273 K in air (Fig.2). The 4 K Mössbauer spectrum of YBaCo$_{3.2}$Fe$_{0.8}$O$_{7+\delta}$ displays sextets with parameters characteristic of tetrahedral Fe$^{3+}$, nearly identical to those observed for YBaCo$_{3.96}$Fe$_{0.04}$O$_{7+\delta}$ in spite of a slightly different Fe$^{3+}$ site distribution (Table 1). These sextets appear at $T_{\text{MF}} \approx 60$ K, lower than $T_{\text{MF}} \approx 73$ K for YBaCo$_{3.96}$Fe$_{0.04}$O$_{7+\delta}$. In addition, YBaCo$_{3.2}$Fe$_{0.8}$O$_{7+\delta}$ spectrum exhibits a third sextet with relatively high IS and $B_{\text{hf}}$ characteristic of octahedrally-coordinated Fe$^{3+}$ in perovskite-related oxides (Fig.8). For instance, the IS and $B_{\text{hf}}$ values of Fe$^{3+}$ cations in YFeO$_3$ are 0.45 mm/s and 54.7 T, respectively; in the case of BaFeO$_{3.4}$, IS = 0.48 mm/s and $B_{\text{hf}} = 50$ T. Moreover, the sextet with high IS and $B_{\text{hf}}$ in YBaCo$_{2}$Fe$_{0.8}$O$_{7+\delta}$ is kept at room temperature (Fig.9), far from the $T_{\text{MF}}$ of all the other Fe$^{3+}$ states. Such a behavior is opposite with respect to YBaCo$_{3.96}$Fe$_{0.04}$O$_{7+\delta}$ where all the magnetic moments freeze within a narrow temperature range, and can therefore be ascribed to traces of secondary perovskite phase (Fig.1). When considering the relative areas calculated from the Mössbauer spectra (Table 1), the iron solubility limit in the YBaCo$_{4-x}$Fe$_x$O$_{7+\delta}$ structure can thus be estimated as $x \approx 0.7$. One should also note that the Mössbauer spectra of YBaCo$_{3.2}$Fe$_{0.8}$O$_{7+\delta}$ (Fig.8) are very similar to those of YBaCo$_3$FeO$_7$, thus confirming that the high-IS sextet cannot be attributed to any artifacts originating, for example, from materials processing features.
The same sextet remaining up to 295 K is also observed in the spectra of YBaCo$_{3.2}$Fe$_{0.8}$O$_{8.5}$ (Figs. 8 and 9). Apart from this contribution, all the subspectra of oxidized YBaCo$_{3.96}$Fe$_{0.04}$O$_{8.5}$ and YBaCo$_{3.2}$Fe$_{0.8}$O$_{8.5}$ are similar to one another. The estimated $T_{MF}$ values are listed in Table 1.

3.3. Magnetization

The ZFC and FC magnetization vs. temperature curves of YBaCo$_{4-x}$Fe$_{x}$O$_{7+\delta}$ (Fig. 10) are in a good agreement with literature data on YBaCo$_4$O$_7$ for the phases with low and high oxygen content, respectively. In the case of YBaCo$_{3.96}$Fe$_{0.04}$O$_{8.5}$, the ZFC and FC curves both show sharp maxima at the applied field $H = 0.01$ T and critical temperature $T_c \approx 64$ K. When $H$ increases up to 1 T, the maxima broaden. For YBaCo$_{3.2}$Fe$_{0.8}$O$_{7+\delta}$, the FC curve exhibits only a small change in the slope at $T_c \approx 51$ K where the ZFC plot has a maximum. This temperature is significantly lower than that of the undoped cobaltite. The magnetization data on YBaCo$_{4}$O$_{8.5}$ were found virtually identical to YBaCo$_{3.96}$Fe$_{0.04}$O$_{8.5}$, except for a modest decrease (1-2 K) of the critical temperature of the 1% $^{57}$Fe-substituted compound ($T_c \approx 55$ K). Notice also that $T_c$ and $T_{MF}$ values determined from magnetization and Mössbauer data, respectively, all tend to decrease with increasing $\delta$ for undoped and 1% Fe-substituted YBaCo$_{4}$O$_{7+\delta}$, whilst for YBaCo$_{3.2}$Fe$_{0.8}$O$_{7+\delta}$ series an opposite tendency is observed (Table 1).

The temperature dependencies of the reciprocal magnetic susceptibility, Fig. 11, were used to calculate effective magnetic moments ($\mu_{eff}$) by the Curie-Weiss law at 200-300 K. The $\mu_{eff}$ value for YBaCo$_{3.96}$Fe$_{0.04}$O$_{7+0.02}$ (Table 2) is quite close to $\mu_{eff} = 5.44$ $\mu_B$/magnetic atom, reported for YBaCo$_4$O$_7$. Increasing iron concentration at a given oxygen content implies always an increase in $\mu_{eff}$ as expected for the replacement of Fe$^{3+}$ ($S = 5/2$) for Co$^{2+}$ ($S = 3/2$) or Co$^{3+}$ adopting either the high-spin (HS, $S = 2$, $t_{2g}^{3}e_{g}^{2}$), intermediate-spin ($S = 1$, $t_{2g}^{5}e_{g}^{1}$) or low-spin (LS, $S = 0$, $t_{2g}^{6}e_{g}^{0}$) configurations. In fact, recent XAS studies showed that, in YBaCo$_4$O$_7$ and YBaCo$_4$FeO$_7$ where all cobalt-site cations are tetrahedrally-coordinated, Co$^{2+}$ and Co$^{3+}$ are in the HS state. The calculated $\mu_{eff}$ values in the phases with moderate oxygen content (Table 2) are however higher than expected from the experimentally observed $\mu_{eff}$ for HS Co$^{2+}$, Co$^{3+}$ and Fe$^{3+}$ cations in oxides. Taking into account the curvature of the $\chi^{-1}$ vs. $T$ curves below 300 K, this difference may be related to short-range magnetic correlations.

For YBaCo$_{4-x}$Fe$_{x}$O$_{8.5}$ series, the charge neutrality requires that all Co and Fe are trivalent. Considering HS configurations, the oxidation of Co$^{2+}$ into Co$^{3+}$ should increase the average magnetic moment as the number of unpaired electrons in HS Co$^{3+}$ is higher. On the contrary, $\mu_{eff}$ in YBaCo$_{4-x}$Fe$_{x}$O$_{7+\delta}$ display a significant decrease with increasing oxygen content (Table 2), which can only be understood if Co$^{3+}$ cations exist in lower spin states in the oxidized phases. Hexa-coordinated Co$^{3+}$ in oxides is often in the diamagnetic $S = 0$ state while in lower coordination the crystal field may not be strong enough to overcome the spin-pairing energy. For instance, the ground state of octahedrally-coordinated Co$^{3+}$ in (La,A)CoO$_3$ (A = Ca, Sr, Ba) perovskites is non-magnetic, $S = 0$. A transition to
paramagnetic behavior \((S = 1)\) upon heating is caused by the thermal excitation of magnetic spin states.\(^{35-38}\) Tetrahedral coordination leads usually to \(S = 2\), \(S = 1\) or \(S = 2\) states have been suggested by numerous studies on oxides containing CoO\(_5\) pyramids, such as Sr\(_2\)CoO\(_4\)Cl or RBaCoO\(_{5+\delta}\) (R = rare-earth cation, \(\delta = 0-0.5\)).\(^{39-41}\)

Decreasing \(\mu_{\text{eff}}\) with increasing oxygen content suggests, hence, that increasing coordination of Co\(^{3+}\) in YBaCo\(_{4-x}\)Fe\(_x\)O\(_{8.5}\) leads to a decrease in its spin state. However, only a relatively small part (if any) of Co\(^{3+}\) cations in YBaCo\(_{4-x}\)Fe\(_x\)O\(_{8.5}\) may have an \(S = 0\) ground state. In fact, although \(T_c\) and \(T_{\text{MF}}\) tend to decrease with increasing \(\delta\) in YBaCo\(_{3.96}\)Fe\(_{0.04}\)O\(_{7+\delta}\), these transitions do not vanish implying that strong magnetic interactions are still observed and, therefore, a large fraction of Co\(^{3+}\) should have unpaired electrons. Since tetrahedral Co\(^{3+}\) sites would have \(S = 2\) as observed in YBa(Co,Fe)\(_4\)O\(_7\),\(^{18}\) the magnetization data on YBaCo\(_{4-x}\)Fe\(_x\)O\(_{8.5}\) may indicate that oxidation results in the formation of either cobalt-oxygen polyhedra with an \(S = 1\) ground state or with a mixed octahedral \((S = 0)\) and tetrahedral \((S = 2)\) coordination of Co\(^{3+}\). In the former case an octahedral symmetry may hardly be expected even in the case of moderate distortions.\(^{38-40}\) At the same time, the 4 K Mössbauer data show that the fraction of tetrahedrally coordinated Fe\(^{3+}\) in YBaCo\(_{4-x}\)Fe\(_x\)O\(_{8.5}\) is low if any; the average IS values estimated for the main hyperfine field distributions are consistent with predominant 5-fold coordination (Table 1).

### 3.4. Cobalt environments in YBaCo\(_{4}\)O\(_{8.5}\): computer simulations

Statistical analysis of the Co-O distances averaged at each temperature from the MD simulation results, confirmed that all cobalt-oxygen polyhedra in oxidized YBaCo\(_{4}\)O\(_{8.5}\) are strongly distorted. These distortions make it impossible to unambiguously classify the polyhedra into groups each having a definite CN and crystallographic positions, even at low temperatures (Fig.12). In this situation, the most appropriate approach to select major types of the coordination polyhedra is based on the cut-off length for the Co-O bonds. Consideration of the polyhedra fractions vs. cut-off distance (Fig.13A) shows that, for the distances smaller than 2.2-2.3 Å, a significant amount of oxygen anions remains excluded from the main polyhedra and abnormal CN values start to appear. For 2.4-2.5 Å, a tendency to plateau-like behavior is observed for all the cobalt-oxygen polyhedra (CN = 4, 5 and 6). The cut-off length of 2.5 Å was therefore selected to analyze cobalt environments in the entire YBaCo\(_{4}\)O\(_{8.5}\) supercell and in each separate Co-O layer. At this cut-off value and 150 K, the average Co-O bond lengths in the tetrahedra, pyramids and octahedra are 1.7772, 1.8670 and 1.9542 Å, respectively. If compared to other polyhedra, the pyramids (CN = 5) are dominant in YBaCo\(_{4}\)O\(_{8.5}\) lattice in the entire temperature range (Figs.13 and 14), in agreement with the above conclusion regarding prevailing role of 5-fold coordination of Co\(^{3+}\) cations in the structure of oxidized YBa(Co,Fe)\(_4\)O\(_{8.5}\), drawn from the Mössbauer and magnetization data. The remaining tetrahedra and octahedra can hence be considered as defective units formed on structural reconstruction and/or due to thermal fluctuations. Attempts to identify long-range order in the distribution of tetra- and hexa-coordinated cobalt failed, except for a
tendency for the preferential octahedra location in the $Co_2$-O layers corresponding to Kagomé-type sheets in the YBaCo$_4$O$_{7+\delta}$ structure. Typical examples are presented in Fig. 15 and in ESI†. While the location of cobalt-oxygen tetrahedra and octahedra is essentially random (Table 3), the metal sites retain overall long-range ordered arrangement (Fig. 15) that explains why the oxidized phases ($\delta$~1-1.5) appear crystalline in neutron powder diffraction data.$^{12,14}$ Another necessary comment is that the overall degree of the oxidation-induced disorder in YBaCo$_4$O$_{7+\delta}$, revealed by the MD simulations, is substantially higher compared to other layered oxide systems, such as K$_2$NiF$_4$-type La$_2$(Ni,M)O$_{4+\delta}$ (M = Fe, Co, Cu).$^{24}$ This correlates with specific features of the Kagomé-type structure comprising the layers of corner-sharing CoO$_4$ tetrahedra, and with the relatively low thermodynamic stability of YBaCo$_4$O$_{7+\delta}$.

The picture of highly disordered oxygen sublattice resulting from the MD simulations is also consistent with the TEM observations,$^{15}$ which showed several types of structural modulations and reversible transitions between them in YBaCo$_4$O$_{8.5}$. The TEM results$^{15}$ suggest, in particular, that the local structure may have six-fold or lower symmetry, depending on the oxygen ordering type. One should also mention that possible presence of cobalt-oxygen pyramids should probably be considered even for the YBaCo$_4$O$_8$ lattice. As an example, one peak corresponding to the $2\theta$ angle of approximately 42.4º (CuK$_\alpha$ radiation), observed also in the present work and indicated by the arrow in Fig. 1, is apparently poorly described by the $Pbc\overline{2}1$ superstructure.$^{12}$

In addition to the dominant structural units in oxidized YBaCo$_4$O$_{7+\delta}$, the simulation results indicate another important tendency, namely, very unusual volume expansion when moderate amounts of oxygen are intercalated (Table 4). Such expansion is likely to be the result of opposite effects of decreasing ionic radius of cobalt on oxidation from Co$^{2+}$ to Co$^{3+}$ and its increasing coordination number. The same factors seem responsible for the anisotropic behavior of the unit cell parameters on isothermal oxygen uptake (Fig. 5). Whatever the microscopic mechanisms, the chemical expansivity is critical for the potential applications of YBa(Co,Fe)$_4$O$_{7-\delta}$-based materials for ceramic membranes$^{42}$ and fuel cell cathodes$^{33}$.

### 3.5. Chemically induced strains

Dimensional instabilities under large oxygen chemical potential gradients and/or under $p$(O$_2$) variations are typical for perovskite-like cobaltites, such as (La, Sr)CoO$_3$.$^{44,45}$ Oxygen losses from the perovskite lattice and the resultant increase of the cobalt cation radius lead to unfavorable lattice expansion on reduction and differential strain across the membrane; similar processes occur in the porous cathodes under high current densities. All these nonstoichiometry changes induce stresses that may cause mechanical degradation and fracture. For perovskite
cobaltites, substantially high chemical strains appear usually above 900 K. In the case of YBa(Co,Fe)$_3$O$_{7+\delta}$, extensive oxygen sorption starts at considerably lower temperatures (Fig.2).

Fig.16A presents one example of isothermal dilatometric curve of dense YBaCo$_4$O$_{7+\delta}$ ceramics, collected in air at 598 K. Prior to the measurements, the sample containing approximately 7 oxygen atoms per formula unit was heated up to 598 K at a rate of 5 K/min. A slow isothermal expansion is clearly observed due to progressive oxygen intercalation (cf. Figs. 2A, 5 and 16A). The total elongation with respect to room temperature is ~0.5%. When the atmosphere is switched to flowing oxygen, the ceramic length further increases by almost 0.25 % (Fig.16B). Reducing $p(O_2)$ down to 4x10$^{-5}$ atm leads to a substantial contraction. These dimensional variations are reproducible, although the chemical expansion on redox cycling is not completely reversible, reflecting a partial irreversibility of oxygen content variations or/and slow microstructural degradation with time. The same situation was observed for XRPD data due to the redox processes in air (Fig.4).

The dilatometric results seem to agree well with the SLS predictions (Table 4), and with the unit cell volume difference between YBaCo$_4$O$_7$ and YBaCo$_4$O$_{8.1}$ prepared in flowing 20%O$_2$-N$_2$ gas mixture at 603 K for 6 h. At room temperature the difference between the normalized unit cell volumes varies from 0.018% to 0.069% and even 0.13%, confirming the lattice expansion on oxidation. On the other hand, available structural information displays a significant scatter, which partly results from the temperature- and oxidation-induced phase transitions and morphological effects complicating quantitative comparison with the diffraction data.

If compared to perovskite-type cobaltites, the chemical expansivity of YBaCo$_4$O$_{7+\delta}$ ceramics normalized to the oxygen content variations is low. However, the absolute values of chemical strains (Fig.16) are quite similar to those of (La,Sr)CoO$_3$ at elevated temperatures. For instance, on changing the atmosphere between air and N$_2$, the relative linear expansion of La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ ceramics is 0.41% at 1073-1173 K. For YBaCo$_4$O$_{7+\delta}$, a comparable strain level is observed at 598 K (Table 4). Such a behavior implies substantial dimensional instabilities under operating conditions of the ceramic membranes and fuel cell electrodes. These applications require, therefore, extensive doping of YBa(Co,Fe)$_3$O$_{7+\delta}$ with cations having a stable oxidation state in order to suppress lattice reconstruction and volume changes on oxidation.

4. Conclusions

In combination with the computer simulation studies, the magnetization and Mössbauer spectroscopy analyses of YBaCo$_{4-x}$Fe$_x$O$_{7+\delta}$ ($x = 0-0.8$) throw light on the oxidation mechanisms at $\delta \geq 1$, although determination of the relevant crystal structures requires further diffraction experiments. In particular, prevailing formation of (Co,Fe)O$_5$ pyramids and rising local distortions are found very likely in the oxidized YBaCo$_{4-x}$Fe$_x$O$_{7+\delta}$. Strong
magnetic correlations are still observed in YBaCo$_{4-x}$Fe$_x$O$_{8.5}$ whilst the average magnetic moment of Co$^{3+}$ is lower than that in YBaCo$_{4-x}$Fe$_x$O$_{8.5}$ (δ ≤ 0.2). Assuming that octahedrally-coordinated Co$^{3+}$ has $S = 0$ ground state, a large fraction of penta-coordinated Co$^{3+}$ with $S = 1$ ground state should be present in YBaCo$_{4-x}$Fe$_x$O$_{8.5}$, in agreement with predominant 5-fold coordination of Fe$^{3+}$ cations deduced from their average isomer shift. Contrary to the literature reports on single-crystal and polycrystalline YBaCo$_3$FeO$_7$, the iron solubility limit in YBaCo$_{4-x}$Fe$_x$O$_{7+\delta}$ was found to correspond approximately to $x \approx 0.7$. Most likely, this factor is relevant for the different symmetry of YBaFe$_3$O$_7$ phase, which has been recently prepared by annealing in primary vacuum.$^{47}$ The oxygen intercalation in YBaCo$_{4}$O$_{7+\delta}$ at 470-700 K is associated with anisotropic changes in the unit cell parameters and increasing local distortions and disorder. These processes lead to very unusual expansion at moderate oxidation levels, revealed by the controlled-atmosphere dilatometry. In spite of its slow kinetics, such expansivity is undesirable for the electrochemical applications of YBa(Fe,Co)$_4$O$_7$-based ceramic materials and should be suppressed via partial substitution of cobalt in order to avoid the redox-induced structural reconstruction.

Acknowledgements

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17. E.V. Tsipis, V.V. Kharton and J.R. Frade, Solid State Ionics, 2006, 177, 1823.
28. [http://www.ucl.ac.uk/klmc/Potentials/](http://www.ucl.ac.uk/klmc/Potentials/).
† Electronic supplementary information (ESI) available: Selected Mössbauer spectra of YBaCo$_{3.96}$ Fe$_{0.04}$O$_{8.5}$ in the vicinity of $T_{MF}$ and typical distribution of the cobalt-oxygen polyhedra fractions in consecutive layers parallel to the $a$-$b$ plane of simulated YBaCo$_3$O$_{8.5}$, extracted from the MD results at 150 K.
Table 1.

Parameters estimated from the Mössbauer spectra, collected at 295 and 4 K, for YBaCo$_{3.96}$Fe$_{0.04}$O$_{7+x}$ and YBaCo$_{3.2}$Fe$_{0.8}$O$_{7+x}$ with variable oxygen content

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T$, K</th>
<th>IS, mm/s</th>
<th>QS, mm/s</th>
<th>$2\varepsilon$, mm/s</th>
<th>$B_{hf}$, T</th>
<th>$I$, %</th>
<th>CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBaCo$<em>{3.96}$Fe$</em>{0.04}$O$_{7.0}$</td>
<td>4</td>
<td>0.30</td>
<td>-</td>
<td>0.10</td>
<td>44.3</td>
<td>39</td>
<td>4</td>
</tr>
<tr>
<td>$T_{MF} = 73$ K</td>
<td>0.30</td>
<td>-</td>
<td>0.00</td>
<td>41.3</td>
<td>61</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>$T_c = 64$ K</td>
<td>0.18</td>
<td>0.54</td>
<td>-</td>
<td>-</td>
<td>39</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.19</td>
<td>0.37</td>
<td>-</td>
<td>-</td>
<td>61</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>YBaCo$<em>{3.96}$Fe$</em>{0.04}$O$_{7.8}$</td>
<td>4</td>
<td>0.34</td>
<td>-</td>
<td>0.06</td>
<td>44.2</td>
<td>26</td>
<td>5</td>
</tr>
<tr>
<td>$T_{MF} = 70$ K (CN=4)</td>
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<td>-</td>
<td>0.01</td>
<td>42.3</td>
<td>33</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>$T_{MF} = 55$ K (CN=5)</td>
<td>0.31</td>
<td>-</td>
<td>0.10</td>
<td>40.0</td>
<td>41</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>$T_c = 64$ K</td>
<td>0.24</td>
<td>0.96</td>
<td>-</td>
<td>-</td>
<td>28</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.21</td>
<td>0.60</td>
<td>-</td>
<td>-</td>
<td>31</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.31</td>
<td>-</td>
<td>-</td>
<td>41</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>YBaCo$<em>{3.96}$Fe$</em>{0.04}$O$_{8.5}$</td>
<td>4</td>
<td>0.34</td>
<td>-</td>
<td>0.12</td>
<td>41.4</td>
<td>51</td>
<td>5</td>
</tr>
<tr>
<td>$T_{MF} = 55$ K</td>
<td>0.34</td>
<td>-</td>
<td>0.51</td>
<td>39.9</td>
<td>43</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>$T_c = 55$ K</td>
<td>0.34</td>
<td>-</td>
<td>1.28</td>
<td>46.8</td>
<td>6</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.24</td>
<td>0.67</td>
<td>-</td>
<td>-</td>
<td>52</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.23</td>
<td>1.04</td>
<td>-</td>
<td>-</td>
<td>41</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.23</td>
<td>1.51</td>
<td>-</td>
<td>-</td>
<td>7</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>YBaCo$<em>{3.2}$Fe$</em>{0.8}$O$_{7.2}$</td>
<td>4</td>
<td>0.30</td>
<td>-</td>
<td>0.04</td>
<td>44.1</td>
<td>36</td>
<td>4</td>
</tr>
<tr>
<td>$T_{MF} = 60$ K</td>
<td>0.31</td>
<td>-</td>
<td>0.02</td>
<td>41.2</td>
<td>50</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>$T_c = 51$ K</td>
<td>0.47</td>
<td>-</td>
<td>0.20</td>
<td>53.8</td>
<td>14</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.18</td>
<td>0.69</td>
<td>-</td>
<td>-</td>
<td>36</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.18</td>
<td>0.30</td>
<td>-</td>
<td>-</td>
<td>48</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.37</td>
<td>-</td>
<td>0.15</td>
<td>42.9</td>
<td>17</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>YBaCo$<em>{3.2}$Fe$</em>{0.8}$O$_{8.5}$</td>
<td>4</td>
<td>0.35</td>
<td>-</td>
<td>0.13</td>
<td>42.6</td>
<td>57</td>
<td>5</td>
</tr>
<tr>
<td>$T_{MF} = 70$ K</td>
<td>0.35</td>
<td>-</td>
<td>0.72</td>
<td>41.3</td>
<td>27</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>$T_c = 55$ K</td>
<td>0.36</td>
<td>-</td>
<td>1.18</td>
<td>46.3</td>
<td>6</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.47</td>
<td>-</td>
<td>0.23</td>
<td>53.9</td>
<td>13</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.24</td>
<td>0.70</td>
<td>-</td>
<td>-</td>
<td>49</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.22</td>
<td>1.10</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.23</td>
<td>1.52</td>
<td>-</td>
<td>-</td>
<td>8</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.34</td>
<td>-</td>
<td>-0.22</td>
<td>44.3</td>
<td>14</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

Notes:

$T_{MF}$ is the temperature where the effects of slowing down of $\mu_{Fe}$ relaxation below $\sim 10^9$ Hz are observed; $T_c$ is the critical temperature corresponding to the maxima of the ZFC or FC magnetization curves.

IS, $B_{hf}$, QS, $\varepsilon$, and $I$ are the average isomer shift relative to metallic $\alpha$-Fe at 295 K, quadrupole splitting in a quadrupole doublet, quadrupole shift in a magnetic sextet, average magnetic hyperfine field, and relative area, respectively. Estimated standard deviations are $< 2\%$ for $I$, $< 0.2$ T for $B_{hf}$ and $< 0.02$ mm/s for the other parameters.

CN = 5 refers to penta-coordinated Fe$^{3+}$ or to the sum of unresolved contributions with prevailing 5-fold coordination (see text). CN = 6 corresponds to octahedrally-coordinated Fe$^{3+}$ in perovskite-like secondary phase.
Effective magnetic moments of YBaCo$_{4-x}$Fe$_x$O$_{7+\delta}$ and YBaCo$_{4-x}$Fe$_x$O$_{8.5}$

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\mu_{\text{eff}}$, $\mu_B$ per magnetic atom</th>
<th>$\Theta_{\text{CW}}$, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBaCo$<em>{4.4}$Fe$</em>{0.04}$O$_{7+\delta}$</td>
<td>5.44</td>
<td>-907</td>
</tr>
<tr>
<td>YBaCo$<em>{4.4}$Fe$</em>{0.8}$O$_{7+\delta}$</td>
<td>6.76</td>
<td>-1304</td>
</tr>
<tr>
<td>YBaCo$<em>{4.4}$Fe$</em>{x}$O$_{8.5}$</td>
<td>3.34</td>
<td>-157</td>
</tr>
<tr>
<td>YBaCo$<em>{4.4}$Fe$</em>{0.04}$O$_{8.5}$</td>
<td>3.35</td>
<td>-157</td>
</tr>
<tr>
<td>YBaCo$<em>{4.4}$Fe$</em>{0.8}$O$_{8.5}$</td>
<td>4.23</td>
<td>-279</td>
</tr>
</tbody>
</table>

* Data from Ref. 10

Fractions of different Co-O polyhedra in simulated YBaCo$_{4}$O$_{8.5}$ and in the nearest neighborhood of other polyhedra, extracted from the MD results at 150 K*

<table>
<thead>
<tr>
<th>Location</th>
<th>Fractions of given polyhedra</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN = 4</td>
<td>CN = 5</td>
</tr>
<tr>
<td>Entire supercell</td>
<td>0.037</td>
</tr>
<tr>
<td>In the nearest neighborhood of cobalt cations with:</td>
<td></td>
</tr>
<tr>
<td>CN = 4</td>
<td>0.029</td>
</tr>
<tr>
<td>CN = 5</td>
<td>0.036</td>
</tr>
<tr>
<td>CN = 6</td>
<td>0.036</td>
</tr>
</tbody>
</table>

* The cut-off distances are 2.5 Å for the central cation in the polyhedra and 6.0 Å for nearest-neighboring cobalt.

Table 4.

Relative volume changes on oxidation of YBaCo$_{4}$O$_{7+\delta}$, calculated by SLS after lattice relaxation and from the controlled-atmosphere dilatometry results at 598 K

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\Delta V/V_0$, %</th>
<th>$\Delta V/V_{0a}$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBaCo$<em>{4}$O$</em>{8}$</td>
<td>0.91</td>
<td>0.26</td>
</tr>
<tr>
<td>YBaCo$<em>{4}$O$</em>{8.5}$</td>
<td>0.30</td>
<td>1.00</td>
</tr>
</tbody>
</table>

* The relative volume expansion was estimated from the length variations as $\Delta L/L_0 \times 3$. 
Figure captions

Fig.1. XRD patterns of YBaCo$_{3.96}$Fe$_{0.04}$O$_{7+\delta}$ and YBaCo$_{3.2}$Fe$_{0.8}$O$_{7+\delta}$, prepared by quenching after annealing at 1323 K in air and by oxidation at 598 K in air and under 100 atm O$_2$. The rhombs indicate major superstructure reflections. Other marks are explained in the text.

Fig.2. Examples of the oxygen stoichiometry variations in YBaCo$_{4-x}$Fe$_x$O$_{7+\delta}$ at atmospheric oxygen pressure, measured by TGA (see text), and determination of the total oxygen content via reduction into Y$_2$O$_3$, BaO and metallic Co and Fe.

Fig.3. XRPD patterns illustrating phase decomposition of YBaCo$_4$O$_{7+\delta}$ on cooling below 1200 K (A) and phase evolution on heating of metastable YBaCo$_4$O$_{7+\delta}$ (B) at atmospheric oxygen pressure. For (A), the patterns were collected from 1373 to 873 K with isothermal dwells after each 50 K (see text). For (B), the XRPD profiles were obtained on heating from 473 to 1373 K with 20 K steps.

Fig.4. Variations of the hexagonal unit cell parameters of YBaCo$_4$O$_{7+\delta}$ on temperature cycling in air. The powdered sample was preliminarily annealed at 1473 K for 22 h. The measurement regime included consecutive heating up to 773 K with 20 K steps, cooling from 773 to 473 K (50 K steps), and heating from 473 up to 1373 K (20-40 K steps).

Fig.5. Time dependence of the unit cell parameters of YBaCo$_4$O$_{7+\delta}$, preliminarily equilibrated at 1473 K, during isothermal oxygen uptake at 573 K in air.

Fig.6. Mössbauer spectra of YBaCo$_{3.96}$Fe$_{0.04}$O$_{7+\delta}$ collected at 4 K. The samples with $\delta$ = 0.02, 0.80 and 1.5 were prepared by quenching after annealing in air at 1323 K and 598 K, and via oxidation under 100 atm O$_2$ at 598 K, respectively. The lines plotted over the experimental points are the sum of two or three magnetic sextets or magnetic hyperfine field distributions. The subspectra are shown shifted for clarity.

Fig.7. Room-temperature Mössbauer spectra of YBaCo$_{3.96}$Fe$_{0.04}$O$_{7+\delta}$. The lines plotted over the experimental points are the sum of two or three quadrupole doublets. The subspectra are shown shifted for clarity.

Fig.8. Mössbauer spectra of YBaCo$_{3.2}$Fe$_{0.8}$O$_{7+\delta}$, collected at 4 K. The powdered samples with $\delta$ = 0.2 and 1.5 were prepared by quenching after annealing in air at 1323 K and oxidation under 100 atm O$_2$ at 598 K, respectively. The lines plotted over the experimental points are the sum of three magnetic sextets or four magnetic hyperfine field distributions. The subspectra are shown shifted for clarity.
**Fig.9.** Room-temperature Mössbauer spectra of YBaCo$_{3.2}$Fe$_{0.8}$O$_{7+\delta}$. The lines plotted over the experimental points are the sum of two or three quadrupole doublets and one magnetic sextet.

**Fig.10.** Temperature dependencies of the ZFC and FC magnetization ($H = 0.01$ T) for YBa(Co,Fe)$_5$O$_{7+\delta}$ with low (A) and high oxygen hyperstoichiometry (B).

**Fig.11.** Temperature dependencies of reciprocal magnetic susceptibility of YBa(Co,Fe)$_5$O$_{7+\delta}$ measured at $H = 1$ T. Solid and dashed lines correspond to fitting results according to the Curie-Weiss law.

**Fig.12.** View of the simulated YBaCo$_4$O$_{8.5}$ lattice along $c$ axis at 150 K. The supercell (~11600 atoms) was cooled down from $T_{MD} = 1500$ K with 100-200 K steps and equilibration at each temperature.

**Fig.13.** Polyhedra fractions (A) and average Co-O distances in the polyhedra (B) in simulated YBaCo$_4$O$_{8.5}$ at $T_{MD}=150$ K vs. cut-off distance. The cut-off 2.5 Å selected for further analysis is indicated by vertical line dashed. See text for the details.

**Fig.14.** Estimated fractions of various cobalt-oxygen polyhedra in YBaCo$_4$O$_{8.5}$ vs. MD temperature. The cut-off distance is 2.5 Å.

**Fig.15.** Example of the polyhedra distribution in one cobalt-oxygen layer of simulated YBaCo$_4$O$_{8.5}$ at 150 K: side view along the $b$ axis (left) and along $a$ axis (right). Y$^{3+}$ and Ba$^{2+}$ cations are omitted for clarity. The tetrahedra, pyramids and octahedra are shown blue, yellow and red, respectively.

**Fig.16.** Isothermal linear expansion of YBaCo$_4$O$_{7+\delta}$ ceramics on the initial oxidation in air at 598 K (A), and on subsequent redox cycling (B). The reference point corresponds to the sample length after stabilization in air at 598 K.
Fig. 1
Fig. 2
Fig. 3
Fig. 4

Fig. 5
Fig. 6

Fig. 7
Fig. 8

Fig. 9
Fig. 10

Fig. 11
Fig. 12
Fig. 13

Fig. 14
Fig.15
\[ \text{YBaCo}_4\text{O}_{7+\delta} \]
\[ T = 598 \text{ K} \]

Fig. 16