Oxygen Absorption Capability of $YBaCo_4O_{7+\delta}$

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Various powerful oxygenation approaches were tested in order to find the limits of the oxygen-storage capability of $YBaCo_4O_{7+\delta}$. By means of extreme solid-medium high-pressure oxygenation employing $KClO_3$ as an oxygen generator the phase was successfully loaded with excess oxygen up to $\delta \approx 1.56$.

The $YBaCo_4O_{7+\delta}$ phase has a unique ability to reversibly intake/release appreciably large amounts of oxygen at low temperatures.[1] Accordingly the phase is believed to be a promising candidate for an efficient oxygen storage/separator material.[2] In its as-synthesized oxygen-poor ($\delta = 0$) form, $YBaCo_4O_{7+\delta}$ (with the mean oxidation state of cobalt at +2.25) possesses a hexagonal crystal structure that consists of two types of layers of corner-sharing CoO_4 tetrahedra in a 1:3 ratio.[3] Through atmospheric-pressure oxygen annealing at low temperatures it is possible to load the as-synthesized samples with excess oxygen up to $\delta \approx 1.3$.[1] In the present work, a variety of powerful post-synthesis oxidation methods were tested for their capability to oxygenate the $YBaCo_4O_{7+\delta}$ phase. The purpose was to establish the maximum amount of excess oxygen that can be incorporated into the $YBaCo_4O_{7+\delta}$ lattice.

High-pressure (HP) techniques have proven their superiority in stabilizing unusually high oxidation states of transition metals in their oxides.[4] In the present work, we employed two different HP approaches, i.e. gas-medium (10–100 atm O_2) and solid-medium (1–$5\cdot10^4$ atm plus $KClO_3$ as an oxygen generator) treatments. From previous works on various functional cobalt oxide materials, chemical oxidation methods have been found promising as well.[5,6] Therefore, in addition to the HP techniques we tested the capability of a Br_2/H_2O dispersion to oxidize $YBaCo_4O_{7+\delta}$. Moreover, for the sake of comparison normal-pressure annealing experiments in oxygen, air, and nitrogen atmospheres were performed.

The master sample of $YBaCo_4O_{7+\delta}$ was synthesized by an EDTA chelation method.[1] Stoichiometric amounts of Y_2O_3, $Ba(NO_3)_2$, and $Co(NO_3)_2\cdot6H_2O$ were dissolved in a concentrated HNO_3 solution from which the metal ions were chelated with an $EDTA/NH_3$ solution. After evaporating the solvent and burning the residue, the remaining ash was ground, pressed into pellets, and sintered in an N_2 gas flow at 1050 °C for 20 h. From iodometric titration, oxygen content of the thus synthesized XRD-pure $YBaCo_4O_{7+\delta}$ sample (Sample B) was determined at $\delta = 0.13$. A nearly oxygen-stoichiometric sample of $\delta = 0.03$ (Sample A) was obtained by annealing a specimen of Sample B powder in a perfectly air-tight thermobalance (MAC Science TG-DTA 2000S) in flowing N_2 gas at 500 °C for 2 h.

All oxidation experiments were carried out for specimens of Sample B powder. Table 1 summarizes the samples prepared. The chemical oxidation experiment (to obtain Sample C) was performed for a 150-mg specimen in a 20-mL glass vial at room temperature using a 1:1 (in terms of mass) dispersion of Br_2 and H_2O as an oxidation medium for an immersion time of 20 h. Annealing experiments in air (Sample D) and 1 atm O_2 (Sample E) were carried out for 150-mg specimens in a thermobalance at 340 °C for 24 h. Gas-medium HP experiments were carried out for 150-mg specimens in a two-cell-type autoclave at 340 °C for 24 h under oxygen partial pressures of 10 atm (Sample F) and 100 atm (Sample G). For the solid-medium HP experiments a cubic-anvil-type apparatus was used. A 50-mg specimen was mixed with 50–200 mol % of $KClO_3$ and sealed in a gold capsule for HP treatment at 500 °C and 1–$5\cdot10^4$ atm. During such HP treatment $KClO_3$ acts as an efficient in situ oxygen source upon decomposing to KCl (which was then washed out from the product with hot deionized water and ethanol). The best oxygenation result was achieved at $2\cdot10^4$ atm using 125 mol % of $KClO_3$ (Sample H): the lower pressures and/or lower $KClO_3$ contents ended up with samples with lower oxygen contents, whereas application of pressures higher than $2\cdot10^4$ atm was found to destroy the crystal structure without increasing the oxygen content.

For all the samples, A–H, the precise oxygen content was analyzed with an accuracy of ±0.01 by means of three to five parallel iodometric titration experiments.[7] The results are given in Table 1. Chemical oxidation with Br_2 was found clearly less effective than the various annealing techniques in introducing excess oxygen into the $YBaCo_4O_{7+\delta}$ lattice, yielding a δ value as low as 0.38. For the samples annealed in an oxygen-containing atmosphere, the amount of oxygen loaded in the sample was found to increase with increasing oxygen partial pressure. From Table 1, δ values of 1.01, 1.19, 1.32, and 1.46 were obtained when the annealing was performed in 0.2, 1, 10, and 100 atm O_2 gas, respectively. Then, most importantly, for the sample oxygenated by means of the solid-medium HP technique (at $2\cdot10^4$ atm in the presence of 125 mol % of $KClO_3$) a record-high oxygen-content value of $\delta = 1.56$ was reached, which corresponds to the mean Co oxidation state of +3.03.

Table 1. Summary of the present $YBaCo_4O_{7+\delta}$ samples: oxygenation conditions and the resultant oxygen contents, together with the crystal structure data refined in space group $P6_3mc$ for samples A–C and $Pbc2_1$ for samples D–H. The lattice volume V is calculated per one formula unit

Sample	δ	a/Å	b/Å	c/Å	V/Å^3
A: N_2, 1 atm, 500 °C	0.03	6.298	6.298	10.269	176.4
B: as-synthesized	0.13	6.301	6.301	10.243	176.1
C: Br_2/H_2O, 25 °C	0.38	6.276	6.276	10.272	175.2
D: air, 1 atm, 340 °C	1.01	12.755	10.827	10.138	175.0
E: O_2, 1 atm, 340 °C	1.19	12.710	10.888	10.109	174.9
F: O_2, 10 atm, 340 °C	1.32	12.672	10.884	10.101	174.1
G: O_2, 100 atm, 340 °C	1.46	12.689	10.857	10.096	173.9
H: $KClO_3$, $2\cdot10^4$ atm, 500 °C	1.56	12.695	10.899	10.031	173.5

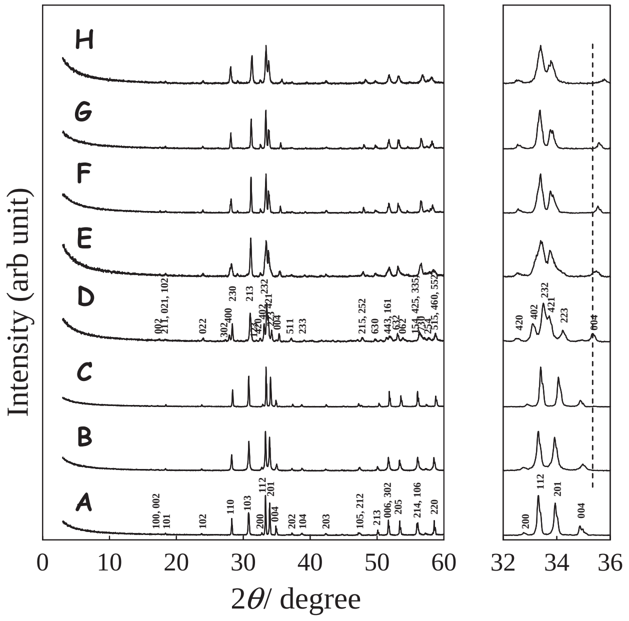

Figure 1. XRD patterns for the present $YBaCo_4O_{7+\delta}$ samples, A–H. Indices are for Sample A (D) in space group $P6_3mc$ ($Pbc2_1$).

All the samples were also characterized by X-ray powder diffraction (XRD) measurements (Rigaku RINT-2000 diffractometer equipped with a rotating Cu anode; Cu Kα radiation), see Figure 1. With increasing oxygen content, i.e., when going from Sample A to Sample H, the 004 reflection about $2\theta = 35°$ is noticeably shifted to higher 2θ angles, as highlighted in the right-hand-side panel of Figure 1.

From the XRD data, the lattice parameters were refined using the software JANA 2000 in the profile-fitting mode. The parent oxygen-stoichiometric $YBaCo_4O_7$ phase is known to crystallize in the hexagonal space group $P6_3mc$.[3] With increasing oxygen content the hexagonal symmetry apparently changes to orthorhombic symmetry.[8] Here we employed space group $P6_3mc$ for the samples with $\delta < 1.0$ and space group $Pbc2_1$ for $\delta \geq 1.0$. The latter space group (with a mixture of tetrahedrally and octahedrally coordinated cobalt) was very recently suggested by Chmaissem et al.[9] on the basis of synchrotron X-ray and neutron powder diffraction data for their sample with $\delta \approx 1.1$. The lattice parameters are given in Table 1. In Figure 2, the c parameter is plotted together with the cell volume V (calculated per one formula unit) against the excess-oxygen content, δ. Both c and V systematically decrease with increasing δ, as a consequence of shrinkage of the ionic radius of cobalt due to oxidation.

To conclude, we were able to load the $YBaCo_4O_{7+\delta}$ lattice with a record-large excess-oxygen amount of $\delta \approx 1.56$ by means of an ultrahigh-pressure oxygenation treatment ($2{\cdot}10^4$ atm, 125 mol % $KClO_3$ as an excess-oxygen source). This is supposed to be close to the maximum value of δ tolerated for the phase, since all our efforts to increase either the pressure or the amount of $KClO_3$ were found to destroy the parent $YBaCo_4O_{7+\delta}$ structure. Additionally, a series of "oxygen-engineered" samples of $YBaCo_4O_{7+\delta}$ was realized (through various oxygenation treatments under milder conditions) to show that the $YBaCo_4O_{7+\delta}$ lattice monotonically contracts upon the oxygen insertion.

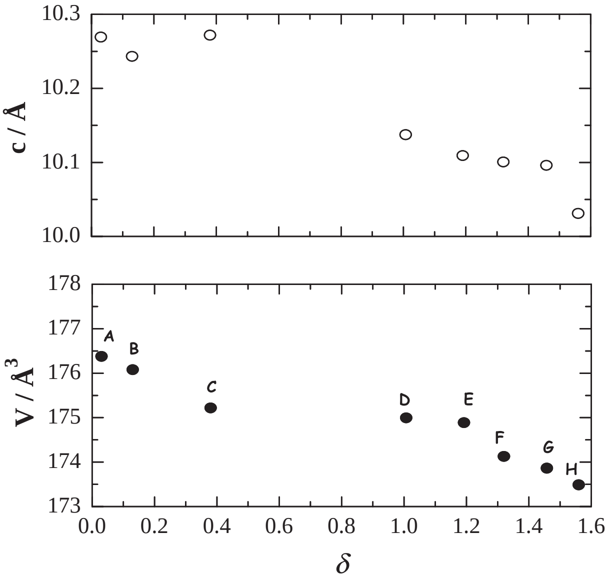

Figure 2. Evolution of the values of lattice parameter c (○) and unit lattice volume V (●) with increasing δ in $YBaCo_4O_{7+\delta}$.

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