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Stoichiometry and copper valence in the $Ba_{1-y}CuO_{2+\delta}$ system

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The cation stoichiometry and the tunability of oxygen content in the $Ba_{1-y}CuO_{2+\delta}$ phase were investigated by means of various methods of chemical analysis. Samples with different nominal metal stoichiometries, y_{nom} ranging from 0 to 0.1, were synthesized. Single-phase samples were obtained for $y_{nom} \approx 0.1$, *i.e.* with about 10 mol% barium deficiency. The possibility to stabilize the $Ba_{1-y}CuO_{2+\delta}$ phase with different oxygen stoichiometries was studied thermogravimetrically. Under an argon atmosphere below 400 °C a part of the excess oxygen of the fully oxygenated $Ba_{0.9}CuO_{2.01}$ sample was found to be released in two steps leading to stoichiometries of $Ba_{0.9}CuO_{1.97}$ and $Ba_{0.9}CuO_{1.94}$. On the other hand, above 400 °C it was possible to continuously tune the oxygen stoichiometry at least down to $Ba_{0.9}CuO_{1.85}$ (700 °C). A decrease in the copper valence with decreasing oxygen content led to an increase in the effective magnetic moment obtained from the magnetic susceptibility measurements performed for two $Ba_{0.9}CuO_{2+\delta}$ samples with different oxygen stoichiometries.

Various mixed oxides of barium, strontium, calcium and copper are utilized as precursor materials for the synthesis of superconducting cuprates. Especially in the ultra-high-pressure synthesis carried out in closed capsules at pressures as high as 2–8 GPa the starting materials should be in oxide form in order to avoid evolution of undesired gases such as carbon dioxide during the decomposition of the precursors. Also, for the stabilization of the superconducting cuprate structures with high-valent copper an excess oxygen source is required.

The $Ba_{1-y}CuO_{2+\delta}$ phase is a promising material as a precursor for the high-pressure synthesis of superconducting cuprates for several reasons. It is a phase providing the desired copper to barium ratio of about 1 : 1. Another advantage is the possibility of having different oxygen stoichiometries in $Ba_{1-y}CuO_{2+\delta}$. In order to control the hole-doping level in the high-pressure synthesized $HgBa_2Ca_2Cu_3O_{9-\delta}$ (Hg-1223) as well as in various other new M-$m2(n-1)n$ phases, the use of $Ba_{1-y}CuO_{2+\delta}$ precursors providing the excess oxygen has already proven to be advantageous.[1,2] For example, strongly overdoped Hg-1223 samples were obtained by excess-oxygen doping using highly-oxidized $Ba_{1-y}CuO_{2+\delta}$ ($y=0$, $\delta \approx 0.13$) powder in the precursor mixture for the high-pressure synthesis.[1] The less-oxidized, Ar-annealed $Ba_{1-y}CuO_{2+\delta}$ ($y=0$, $\delta \approx 0.06$) yielded a Hg-1223 sample with a different oxygen content and T_c. On the other hand, Loureiro *et al.*[3] correlated the valence of copper in the precursor mixture to the appearance of each member of the $HgBa_2Ca_{n-1}Cu_nO_{3+2n\pm\delta}$ homologous series.

Thus, the redox state of the precursor material is important in the synthesis of superconducting materials of controlled oxygen content and structure. Various oxygen stoichiometries, usually in the range of $0<\delta<0.13$, have been proposed for the $Ba_{1-y}CuO_{2+\delta}$ phase. In these studies the chemical analyses for the oxygen content are mostly performed for powders with $y=0$. On the other hand, there are several reports on the possibility of cation non-stoichiometry in the $Ba_{1-y}CuO_{2+\delta}$ phase, many of the papers proposing that the phase is barium deficient.[4–7] Furthermore, no detailed information on the possible range and conditions for tuning the oxygen stoichiometry has been published.

The possible non-stoichiometry in the $Ba_{1-y}CuO_{2+\delta}$ phase is likely to be related to the complexity of the structure. The structure was for the first time described by Kipka and Müller-Buschbaum[8] in 1977 as cubic *Im*3*m* with a lattice constant of ≈18.27 Å. In the unit cell, containing 360 atoms and 90 formula units, each chemical species occupies several different chemical environments. The structure studies by Paulus[4,5] suggested a stoichiometry of $Ba_{0.92}Cu_{1.06}O_{2.28}$ for the phase indicating large deviations from the ideal composition. In some papers it has been proposed that the CO_3^{2-} ion is required to stabilize the structure,[9,10] although formation of $Ba_{0.89}CuO_{2+\delta}$ in carbonate-free conditions has been reported as well.[6]

The aim of the present study was to establish the possible cation and oxygen stoichiometries of $Ba_{1-y}CuO_{2+\delta}$ by means of chemical analysis. In order to study the cation stoichiometry several $Ba_{1-y}CuO_{2+\delta}$ samples with different Ba : Cu ratios were synthesized. For checking the phase-purity of the samples both X-ray diffraction (XRD) and thermogravimetry (TG) were used. The tunability of the oxygen stoichiometry was studied by various annealing experiments carried out in a thermobalance. The oxygen contents in the as-synthesized and post-annealed samples were determined with three different methods: iodometric titration, Cu(I)/(II) coulometric titration and thermogravimetric H_2-reduction. From these three methods, iodometric titration and H_2-reduction are the most common ones for determining higher oxidation states of transition metal ions in their oxides and they have also been widely used for the analysis of the oxygen contents in various high-T_c cuprate superconductors.[11,12] The coulometric Cu(I)/(II) titration method has so far not been applied for the analysis of $Ba_{1-y}CuO_{2+\delta}$, but has proven to be a powerful technique for the oxygen content analysis of various other mixed copper oxides.[13–15] The accuracy for the oxygen content values obtained by the two titration methods is ±0.01 while the TG-reduction method gives somewhat less accurate results (±0.05).[11,12] Finally, magnetic susceptibility *versus* temperature dependence was measured from two samples with different oxygen stoichiometries in order to determine the changes in the electron configuration of copper during the oxidation and reduction processes.

Experimental

The $Ba_{1-y}CuO_{2+\delta}$ samples were prepared by a solid state reaction technique from BaO_2 (Baker) and CuO (Merck) powders of analytical grade. Since BaO_2 is sensitive to H_2O and CO_2 forming compounds such as $Ba(OH)_2 \cdot 8H_2O$ and $BaCO_3$, the purity of the BaO_2 powder was analyzed prior to use. The powder was first checked thermogravimetrically (Perkin-Elmer System 7 TGA) by heating (2 °C min^{-1}) a sample of *ca.* 35 mg to 700 °C in argon. BaO_2 was found to decompose at *ca.* 520 °C to form BaO. The peroxide content of the BaO_2 powder was estimated from the observed weight loss, which turned out to be significantly smaller than the calculated weight loss in pure BaO_2. Assuming the rest of the powder to be $BaCO_3$ ($BaCO_3$ decomposes at higher temperatures) the composition of the used precursor was written as $0.828\ BaO_2 + 0.172\ BaCO_3$. (Based on the results of preliminary thermogravimetric experiments $BaCO_3$ decomposes under the synthesis conditions. This ensures the desired barium stoichiometry in the samples but leaves, however, some ambiguity in terms of possible carbon contamination in the $Ba_{1-y}CuO_{2+\delta}$ phase. With the available chemical analysis techniques it was not possible to either exclude or conclude the carbon contamination.) The barium content of the powder was further checked by EDTA-titration, and the titration result agreed well with the composition obtained from the thermogravimetric experiment.

Fully oxidized $Ba_{1-y}CuO_{2+\delta}$ samples were synthesized with six different Ba : Cu stoichiometries, *i.e.* $y_{nom} = 0$, 0.025, 0.05, 0.075, 0.1 and 0.33. Additionally the barium-rich phase $Ba_2CuO_{3+\delta}$ with a Ba : Cu ratio of 2 : 1 was prepared. The powder mixtures of appropriate amounts of the raw materials were fired in a tube furnace in Al_2O_3 crucibles at 850 °C in flowing oxygen for 20 h. In the case of the $Ba_2CuO_{3+\delta}$ phase a slightly higher temperature of 900 °C was used. The mixtures were reground and the same heat treatment was carried out for the completion of the reaction. The obtained samples were checked for the phase purity by powder X-ray diffraction using a Philips PW1830 powder diffractometer and Cu-Kα radiation. Formation of the reduced phases was studied by various oxygenation/deoxygenation experiments carried out either in a thermobalance or in a tube furnace in a constant flow of oxygen (99.5%) or argon (99.9%). In order to ascertain that the equilibrium conditions in each TG experiment had been achieved the sample (30–40 mg) was kept at the final temperature for 10 hours.

The copper content was analyzed after each annealing procedure by flame atomic absorption spectroscopy (AAS; Perkin Elmer 3100). The samples were dissolved in 0.5 M HCl and two to four parallel determinations of each sample were performed. The mixtures of precursor powders with $y_{nom} = 0.025$ and 0.075 were used as internal standards in the measurement in order to take into account the error possibly caused in the preparation of the standard solutions and weighing the solid samples.

The oxygen contents in all the synthesized single-phase samples were established by the iodometric titration method, *i.e.* by dissolving the sample (30–40 mg) in an acidic solution (0.5 M HCl) containing an excess of KI (*ca.* 1 g). Before the addition of KI, argon was bubbled through the acidic solution for 20 min in order to avoid oxidation of iodide to iodine by the dissolved oxygen. In order to prevent subsequent oxidation by air the titration was carried out in an air-tight cell in an argon atmosphere. Upon dissolving the sample both divalent and trivalent copper are reduced to solid CuI. Also peroxide-type oxygen oxidizes iodide as was confirmed with BaO_2. The iodine formed in the reduction of the samples was titrated by 0.0125 M thiosulfate standardized against CuO of analytical grade.

The level of excess oxygen in the samples was also determined by coulometric Cu(I)/(II) titrations.[11,14] In this method, the possible trivalent copper and/or peroxide-type oxygen are reduced by Cu(I) when dissolving the sample (*ca.* 50 mg) in deoxygenated HCl solution (1 M) containing a known excess of monovalent copper ions (*ca.* 25 mg CuCl). On the other hand, if the sample itself contained monovalent copper, the amount of Cu(I) in the solution would increase upon dissolving the sample. The excess Cu(I) was then determined by a coulometric back-titration ($I = 5$ mA). As for the iodometric titrations, the coulometric titrations were carried out in an argon atmosphere.

The oxygen stoichiometry of the samples was further confirmed by thermogravimetric reduction experiments by heating the sample in a reducing H_2 (5%)–Ar atmosphere up to 950 °C. The amount of oxygen was calculated from the weight loss resulting from the reduction process.[11] In the H_2/TG reduction copper is reduced to the metallic state while barium remains in oxide form. If the sample contained carbonate, it would be released as carbon dioxide in which case the observed weight loss is a sum of the contributions from the amount of both carbonate and excess oxygen. A sample of *ca.* 30–40 mg was weighed in a platinum crucible and the relative weight changes were measured by heating at a rate of 1–2 °C min^{-1}. The slow heating rate was chosen in order to be able to separate the different steps in the step-wise reduction process.

Magnetic measurements were carried out with a SQUID magnetometer (Quantum Design MPMS-5S) in the temperature range 5–300 K. The data as $\chi(\mathrm{emu\ g^{-1}}) = f[T(\mathrm{K})]$ were fitted to the Curie–Weiss equation using a least-square method and the following parameters: the Curie–Weiss temperature θ, the Curie constant C and the temperature independent susceptibility χ_0. From the Curie constant the effective magnetic moment per Cu atom was calculated. The copper mixed oxidation state, *i.e.* the relative amount of Cu(II) and Cu(III) in the sample, was estimated from the effective magnetic moment for two samples with different oxygen stoichiometries.

Results and discussion

Metal stoichiometry

In the $Ba_{1-y}CuO_{2+\delta}$ samples with nominal stoichiometries of $y_{nom} = 0$ and 0.025, small amounts of the unstable $Ba_2CuO_{3+\delta}$ phase were detected by XRD. The presence of this barium-rich phase suggests that the $Ba_{1-y}CuO_{2+\delta}$ phase is barium-deficient, *i.e.* $y > 0.025$, and the excess barium used in the synthesis had partly reacted to form $Ba_2CuO_{3+\delta}$. To obtain pure $Ba_{1-y}CuO_{2+\delta}$ the synthesis was carried out using more barium-deficient precursor mixtures of $y_{nom} = 0.05$, 0.075 and 0.1. Another sample with $y_{nom} = 0.33$ was synthesized for the study of the impurities possibly forming with a strongly barium-deficient precursor stoichiometry. The X-ray diffraction pattern obtained for the $y_{nom} = 0.33$ sample agreed well with those reported for the $Ba_2Cu_3O_{5+\delta}$ by Thompson *et al.*[16] and Brosha *et al.*[17] The samples with $y_{nom} = 0.05$, 0.075 and 0.10 were found to be phase-pure $Ba_{1-y}CuO_{2+\delta}$ within the detection limit of XRD. However, in the sample with $y_{nom} = 0.05$ some elevation in the baseline was observed around the 2θ angles corresponding to the strongest reflections of the $Ba_2CuO_{3+\delta}$ phase. Some of the strong diffraction peaks of $Ba_2Cu_3O_{5+\delta}$ overlap with those of $Ba_{1-y}CuO_{2+\delta}$. Thus, identification of trace amounts of $Ba_2Cu_3O_{5+\delta}$ in the $Ba_{1-y}CuO_{2+\delta}$ samples by XRD is not straightforward.

The possible impurity phases, $Ba_2CuO_{3+\delta}$ and $Ba_2Cu_3O_{5+\delta}$, were also characterized in a thermobalance. The behaviour of these phases in the used heat treatments was found to be different from that of $Ba_{1-y}CuO_{2+\delta}$, and their presence in the $Ba_{1-y}CuO_{2+\delta}$ samples could be detected thermogravimetrically even below the detection limit of XRD. The barium-rich $Ba_2CuO_{3+\delta}$ phase started to react around 120 °C with the moisture or CO_2 impurities present in the used Ar-atmosphere. The weight gain at 120 °C was clearly seen in the sample with $y_{nom} = 0$ and it was also detected in the $y_{nom} = 0.025$ sample.

On the other hand, in the sample with $y_{nom}=0.05$ a small weight change occurred around 220 °C. According to Maiorova *et al.*[18] the weight loss at 220 °C is due to the loss of water from $Ba(OH)_2{\cdot}8H_2O$. The excess of oxygen in the $Ba_2Cu_3O_{5+\delta}$ phase is released at *ca.* 600 °C where the $Ba_{1-y}CuO_{2+\delta}$ phase has weight changes as well. The weight loss of $Ba_2Cu_3O_{5+\delta}$ at this temperature is, however, so sharp that even small amounts of $Ba_2Cu_3O_{5+\delta}$ as an impurity phase in $Ba_{1-y}CuO_{2+\delta}$ would be detected thermogravimetrically.

According to X-ray diffraction and thermal analysis no CuO, BaO_2, $Ba_2CuO_{3+\delta}$ or $Ba_2Cu_3O_{5+\delta}$ were present in the samples with $y_{nom}=0.075$ and 0.10. This is a clear manifestation of the non-stoichiometry in the $Ba_{1-y}CuO_{2+\delta}$ phase in terms of metal composition since pure samples were obtained only with rather large barium deficiency. The result is in good agreement with the study of Wong-Ng and Cook[6] who investigated phase diagrams of different cuprate systems and reported the cation stoichiometry of the $Ba_{1-y}CuO_{2+\delta}$ phase to be $Ba_{0.89}CuO_{2+\delta}$. Consistently, Paulus[4,5] reported, based on the structural study by X-ray diffraction, the stoichiometry of the phase to be $Ba_{0.87}CuO_{2+\delta}$. With the characterization methods applied in the present study it was impossible to decide which one of the samples, $y_{nom}=0.075$ or 0.10, was better. However, the sample with $y_{nom}=0.10$ was chosen for the further characterization. The amount of excess oxygen in the as-synthesized $Ba_{0.9}CuO_{2+\delta}$ sample was determined by iodometric titration as $2+\delta=2.01\pm0.01$. This corresponds to an average copper-valence value of +2.22.

Oxygen stoichiometry

The possibility to stabilize the $Ba_{0.9}CuO_{2+\delta}$ phase with oxygen contents lower than the case of $\delta=0.01$, as obtained when synthesizing the phase in an oxygen atmosphere, was studied with argon annealings carried out in a thermobalance at different temperatures. When the oxidized $Ba_{0.9}CuO_{2+\delta}$ sample was annealed in an argon atmosphere, the weight loss was found to start at about 330 °C, as seen from the thermogram in Fig. 1. Parallel isothermal annealings at 330 °C for 10 h resulted reproducibly in a weight loss of 0.25–0.3%, *i.e.* in the stoichiometry $Ba_{0.9}CuO_{1.97}$. This product corresponds to one of the stable oxygen stoichiometries since several reduction experiments in a temperature range 330–370 °C ended up with the same weight loss, as shown in Fig. 2. On the other hand, in the isothermal annealings at 390 °C a total oxygen loss of *ca.* 0.45% was observed corresponding to the reduction of $Ba_{0.9}CuO_{2.01}$ to $Ba_{0.9}CuO_{1.94}$. The $Ba_{0.9}CuO_{1.94}$ compound is another stable oxygen stoichiometry in the $Ba_{0.9}CuO_{2+\delta}$ series. Note that, the weight change between the stoichiometries of the present $Ba_{0.9}CuO_{2.01}$ and $Ba_{0.9}CuO_{1.94}$ samples agrees with the difference (*ca.* 0.48%) between the molecular weights of the often reported oxidized ('$BaCuO_{2.13}$') and reduced ('$BaCuO_2$') forms of $Ba_{1-y}CuO_{2+\delta}$ powder with $y=0$.[1,19]

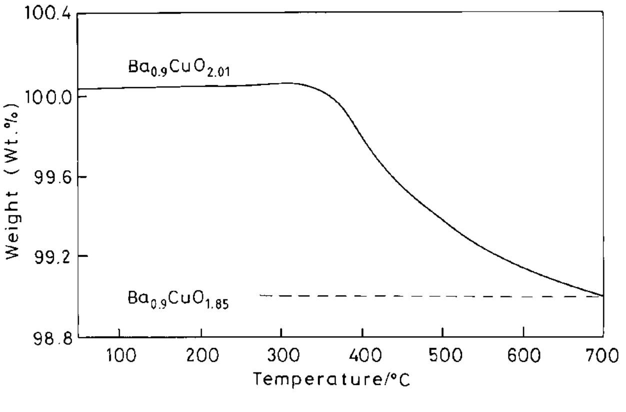

Fig. 1 TG curve for the reduction of $Ba_{0.9}CuO_{2.01}$ in an argon atmosphere up to 700 °C measured with a heating rate of 2 °C min^{-1}.

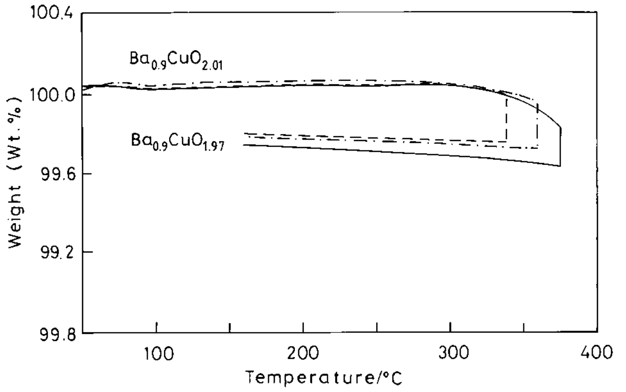

Fig. 2 TG curves for the isothermal reductions of $Ba_{0.9}CuO_{2.01}$ in an argon atmosphere at temperatures of 330 °C (– –), 355 °C (— • —) and 370 °C (—).

At about 400 °C a change in the slope is observed for the weight loss curve recorded for the oxidized $Ba_{0.9}CuO_{2+\delta}$ sample in an argon atmosphere (Fig. 1). Above 400 °C the weight/oxygen content decreases in a more gentle way, which suggests that the oxygen is released in a more continuous manner at higher temperatures. In order to corroborate this, two $Ba_{0.9}CuO_{2+\delta}$ samples were prepared by annealing the oxidized material isothermally at temperatures of 500 and 700 °C in an argon atmosphere. The annealings were carried out in a tube furnace for 15 h. Iodometric titration of these two reduced bulk samples resulted in the same oxygen content values as were detected *in situ* at the temperatures of 500 and 700 °C, confirming that the reduction thermogram shown in Fig. 1 corresponds to the equilibrium state at temperatures above 400 °C. Furthermore, the observed increases in weight/oxygen content during the oxygenation of the two argon-annealed samples agree reasonably well with the result of the chemical analysis. The oxidation curves of all the argon-annealed, partially reduced $Ba_{0.9}CuO_{2+\delta}$ samples are shown in Fig. 3. Table 1 summarizes the results from the experiments of tuning the copper valence in $Ba_{0.9}CuO_{2+\delta}$ by argon

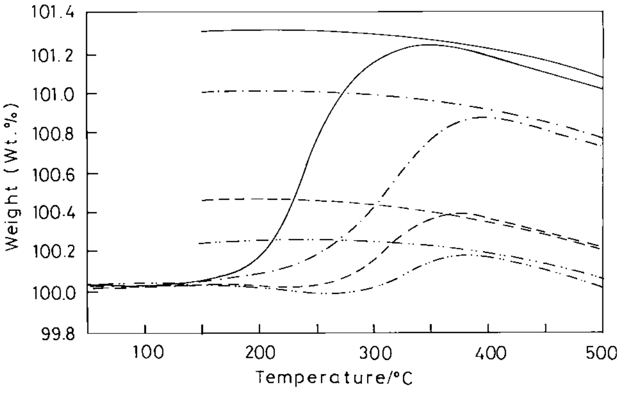

Fig. 3 TG curves for the oxidation of $Ba_{0.9}CuO_{1.85}$ (—), $Ba_{0.9}CuO_{1.92}$ (— • —), $Ba_{0.9}CuO_{1.94}$ (– –) and $Ba_{0.9}CuO_{1.97}$ (— • • —) in an oxygen atmosphere measured with a heating rate of 1 °C min^{-1}.

Table 1 Oxygen stoichiometry of $Ba_{0.9}CuO_{2+\delta}$ after argon annealings at different temperatures

Formula	Annealing temperature/ °C
$Ba_{0.9}CuO_{1.97}$	330–370
$Ba_{0.9}CuO_{1.94}$	380
$Ba_{0.9}CuO_{1.92}$	500
$Ba_{0.9}CuO_{1.85}$	700

Table 2 Oxygen stoichiometries and the corresponding copper valence values of the $Ba_{0.9}CuO_{2+\delta}$ samples as determined by iodometric and coulometric titrations

Sample	Oxygenated	Ar-annealed (500 °C)	Ar-annealed (700 °C)
δ, iodometric	−0.012	0.084	−0.149
Cu-valence	+2.225	+2.032	+1.901
δ, coulometric	0.040	—	−0.139
Cu-valence	+2.280	—	+1.922

annealings at different temperatures. The AAS results for the copper contents confirm that no significant changes occurred in the metal stoichiometry of the samples during the long annealing periods in argon.

The as-synthesized and the reduced $Ba_{0.9}CuO_{2+\delta}$ samples were titrated iodometrically several times in order to obtain reliable results for the oxygen contents. The oxygen contents obtained from the iodometric titration for the present $Ba_{0.9}CuO_{2+\delta}$ samples result in formulae of $Ba_{0.9}CuO_{2.01}$ for the as-synthesized sample, $Ba_{0.9}CuO_{1.92}$ for the sample Ar-annealed at 500 °C and $Ba_{0.9}CuO_{1.85}$ for the sample Ar-annealed at 700 °C. The oxidized $Ba_{0.9}CuO_{2.01}$ sample has some trivalent copper and the $Ba_{0.9}CuO_{1.85}$ sample obtained with Ar-annealing at 700 °C has a copper mixed valence below +II. If the oxygen stoichiometry had been calculated without taking the barium deficiency into account the results would lead to the formulae of '$BaCuO_{2.16}$' for the as-synthesized sample and '$BaCuO_{2.05}$' and '$BaCuO_{2.00}$' for the samples annealed in argon at 500 and 700 °C, respectively. The results agree well with the reported oxygen contents, *i.e.* copper mixed oxidation states for the $BaCuO_{2+\delta}$ phase assumed to be stoichiometric in respect to the cations.[1,19] The oxygen contents and the mixed valences of copper in each sample as calculated from the results of chemical analysis are collected in Table 2. The coulometric titration gave somewhat higher values than the iodometric titration method but the difference was, however, so small that the results from the two methods could be considered to be in good agreement with each other.

The TG curves for the H_2 reduction of the $Ba_{0.9}CuO_{2+\delta}$ samples are shown in Fig. 4. The total weight losses obtained were 9.5% for the oxygenated sample and 8.8 and 8.0% for the samples annealed in argon at 500 and 700 °C, respectively. Thermogravimetric reduction gave systematically the highest oxygen content values. The same systematic shift has been previously observed for $CuBa_2YCu_2O_{7-\delta}$ and has been explained by a presence of small amounts of carbonate.[11,12] On the other hand, the accuracy and reproducibility of the thermogravimetric reduction method are not as good as in the titration methods thus leaving some ambiguity in the interpretation of the reduction results. Even though the possible carbonate contamination would slightly affect the absolute oxygen content values of the $Ba_{0.9}CuO_{2+\delta}$ samples, it would not change the present conclusions for the possibility to control the oxygen stoichiometry.

The first H_2 reduction step is quite different in magnitude in the $Ba_{0.9}CuO_{2+\delta}$ samples with different oxygen stoichiometries. As in the case of $CuBa_2YCu_2O_{7-\delta}$ the first step seems to correspond to a liberation of the removable oxygen in the structure. This weight loss correlates with the occupation of a certain oxygen site in the $Ba_{0.9}CuO_{2+\delta}$ structure, as will be discussed elsewhere based on powder neutron diffraction data obtained for samples with three different oxygen stoichiometries.[20] In the case of the reduction of $CuBa_2YCu_2O_{7-\delta}$ the final weight loss at *ca.* 700 °C was related to the reduction of $YCuO_2$ [containing Cu(I)] to metallic copper and yttrium oxide.[11] Similarly, the reduction at *ca.* 700 °C observed in the present study may originate from the reduction of monovalent copper in a mixed-oxide environment.

Magnetic susceptibility

Copper(II) compounds always have some paramagnetic character due to the $3d^9$ and $S=1/2$ configuration of Cu(II). Copper(III) has $3d^8$ configuration and depending on the chemical environment the electrons on the 3d core can arrange differently. In the high spin case (both d_{z^2} and $d_{x^2-y^2}$ half-filled) Cu(III) is paramagnetic with $S=1$. In the low spin case the two e_g electrons are both in d_{z^2} and the atom is diamagnetic ($S=0$). Most Cu(III) compounds are found to be diamagnetic. In such a low spin case the mixed oxidation number and the presence of Cu(III) can be estimated from the observed decrease in the effective magnetic moment.

The fully oxygenated $Ba_{0.9}CuO_{2.01}$ sample and the $Ba_{0.9}CuO_{1.92}$ sample annealed in argon at 500 °C were chosen for magnetic susceptibility measurements. The magnetic susceptibility of both samples followed the Curie–Weiss law in the temperature range of 80–300 K. The fitted molar susceptibility curves with observed and calculated points are shown in Fig. 5. There is a clear difference between the molar susceptibility curves of the oxygenated and argon-annealed samples. Since the molar magnetic susceptibility decreases with an increase in the oxidation state of copper it can be stated that the Cu(III) 3d electronic configuration in the oxidized sample is mainly of low spin. The values obtained from the fit of the Curie–Weiss equation are shown in Table 3. The theoretical 'spin only' magnetic moment of Cu(II) is 1.73 μ_B but typically the observed values for the Cu(II) magnetic moment are in the range of 1.7–2.2 μ_B due to small changes in the *g*-factor.[21] Therefore it was considered more reasonable to compare the values of effective magnetic moments of the fully oxidized and reduced $Ba_{0.9}CuO_{2+\delta}$ samples rather than to compare these values to the 'spin only' value of Cu(II). From the chemical

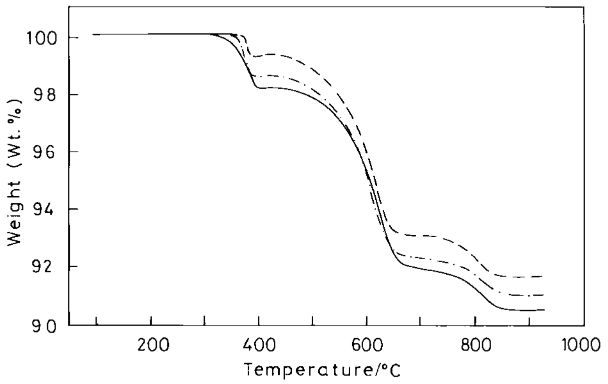

Fig. 4 TG curves for the reduction of $Ba_{0.9}CuO_{2.01}$ (—), $Ba_{0.9}CuO_{1.92}$ (— • —) and $Ba_{0.9}CuO_{1.85}$ (--) in a 5% H_2–95% Ar atmosphere measured with a heating rate of 2 °C min^{-1}.

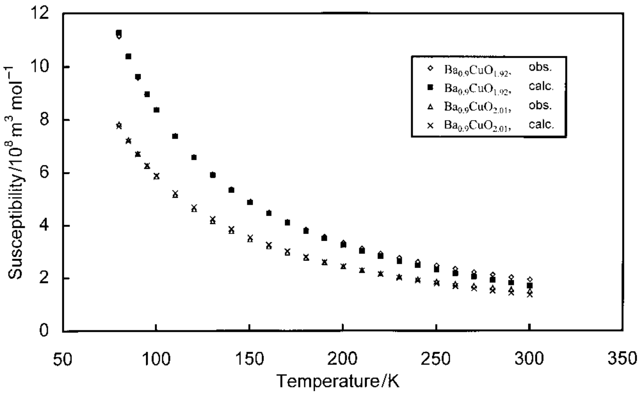

Fig. 5 Molar susceptibility *versus* temperature curves for the oxygenated sample and the sample annealed in Ar at 500 °C.

Table 3 Curie–Weiss fitting parameters for the magnetic susceptibility data and the average copper valence values calculated from both the obtained effective magnetic moments and the chemical analysis data

Sample	$Ba_{0.9}CuO_{2.01}$	$Ba_{0.9}CuO_{1.92}$
θ/K	9.72	14.33
10^6 C/m^3 K mol^{-1}	0.594	0.818
10^8 χ_0/m^3 mol^{-1}	-0.691	-1.160
μ_{eff}/μ_B	1.94	2.28
$(\mu_{eff}/2.315)^2$	0.705	0.971
Cu-valence (susc.)	+2.29	+2.03
Cu-valence (chem.)	+2.22	+2.03

analysis the average valence of copper in the reduced sample was found to be close to +II, *i.e.* +2.03. Assuming this value for the copper valence in the reduced sample, a copper-valence value of +2.29 was deduced from the susceptibility data (Table 3) for the oxidized sample. This value is in good agreement with the value established by chemical analysis (+2.22).

Conclusions

The present study has shown the $Ba_{1-y}CuO_{2+\delta}$ phase to be *ca.* 10 mol% barium deficient. The obtained formula for the phase-pure material synthesized under an oxygen atmosphere was $Ba_{0.9}CuO_{2.01\pm0.03}$ corresponding to the average copper valence of +2.22. Below a temperature of *ca.* 400 °C the excess oxygen of the fully oxygenated sample was released in an argon atmosphere in two steps, while above 400 °C it was possible to tune the oxygen stoichiometry in a continuous way at least down to $Ba_{0.9}CuO_{1.85}$ (700 °C). The possible carbonate contamination of the $Ba_{0.9}CuO_{2+\delta}$ samples does not affect these conclusions although absolute oxygen content values might be slightly shifted. The oxygen stoichiometries were determined by iodometric and coulometric titrations as well as by thermogravimetric H_2-reduction. The magnitude of the first step in the H_2-reduction curves was found to be dependent on the oxygen content of the sample. Therefore, the first step could possibly be used alone for the determination of the oxygen content in $Ba_{0.9}CuO_{2+\delta}$ samples. In addition to the chemical analysis of the oxygen stoichiometries in the oxygenated $Ba_{0.9}CuO_{2+\delta}$ and Ar-annealed (500 °C) samples, the change in the copper valence was followed by magnetic susceptibility measurements. The measurement showed the trivalent copper in the oxygenated sample to have mainly low-spin configuration. The estimations for the copper valency obtained from susceptibility measurements were in good agreement with the results of chemical analysis.

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References

1 K. Fujinami, T. Ito, H. Suematsu, K. Matsuura, M. Karppinen and H. Yamauchi, *Phys. Rev. B*, 1997, **56**, 14790.
2 T. Ito, H. Suematsu, M. Karppinen and H. Yamauchi, *Physica C*, in press.
3 S. M. Loureiro, C. Stott, L. Philip, M. F. Gorius, M. Perroux, S. Le Floch, J. J. Capponi, D. Xenikos, P. Toulemonde and J. L. Tholence, *Physica C*, 1996, **272,** 94.
4 E. F. Paulus, *J. Solid State Chem.*, 1991, **90,** 17.
5 E. F. Paulus, *Z. Kristallogr.*, 1994, **209,** 586.
6 W. Wong-Ng and L. P. Cook, *Physica B*, 1996, **273,** 135.
7 W. Wong-Ng and L. P. Cook, *Powder Diffr.*, 1994, **9,** 280.
8 R. Kipka and H. Müller-Buschbaum, *Z. Naturforsch.*, *Teil B*, 1977, **32**, 121.
9 M. A. G. Aranda and J. P. Attfield, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32,** 1454.
10 Y. Y. Skolis and M. L. Kovba, *5th International Workshop*: *High-Temperature Superconductors and Novel Inorganic Materials Engineering* (*MSU-HTSC V*), March 24–29, 1998, Moscow, Russia. Abstracts, p. 25.
11 M. Karppinen, A. Fukuoka, L. Niinistö and H. Yamauchi, *Supercond. Sci. Technol.*, 1996, **9**, 121.
12 M. Karppinen and L. Niinistö, *Supercond. Sci. Technol.*, 1991, **4**, 334.
13 G. Kawamura and M. Hiratani, *J. Electrochem. Soc.*, 1987, **134**, 211.
14 K. Kurusu, H. Takami and K. Shintomi, *Analyst*, 1989, **114**, 1341.
15 M. Karppinen, H. Yamauchi and S. Tanaka, *J. Solid State Chem.*, 1993, **104**, 276.
16 J. G. Thompson, J. D. Fitz Gerald, R. L. Withers, P. J. Barlow and S. Anderson, *Mater. Res. Bull.*, 1989, **24**, 505.
17 E. L. Brosha, H. G. Fernando and I. D. Raistrick, *J. Solid State Chem.*, 1998, **122**, 176.
18 A. F. Maiorova, S. N. Mudretsova, S. F. Pashin and M. A. Bykov, *Thermochim. Acta*, 1992, **197**, 219.
19 M. T. Weller and D. R. Lines, *J. Solid State Chem.*, 1989, **82**, 21.
20 K. Peitola, M. Karppinen, H. Rundlöf, R. Tellgren, H. Yamauchi and L. Niinistö, *J. Mater. Chem.*, to be submitted.
21 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, John Wiley, London 1980, 4th edn., p. 628.

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