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Structural changes related to changes in oxygen stoichiometry in the $Ba_{1-y}CuO_{2+\delta}\cdot(CO_2)_x$ system as determined by powder X-ray and neutron diffraction

Kaisa Peitola,[a] Maarit Karppinen,*[a,b] Håkan Rundlöf,[c] Roland Tellgren,[c] Hisao Yamauchi[b] and Lauri Niinistö[a]

[a]Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology, FIN-02015 Espoo, Finland. E-mail: mjkarppi@pop.hut.fi
[b]Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan
[c]Inorganic Chemistry, Ångström Laboratory, Uppsala University, S-75121 Uppsala, Sweden

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Structural changes related to changes in the oxygen stoichiometry $2+\delta$ in the mixed-valent cuprate '$BaCuO_{2+\delta}$' have been studied by means of X-ray and neutron powder diffraction techniques. The cubic structure of '$BaCuO_{2+\delta}$' with space group *Im*3*m* consists of partially and fully occupied parts with metal atoms in several different crystallographically equivalent positions. Three samples with stoichiometries of $Ba_{0.9}CuO_{2.02}\cdot(CO_2)_x$, $Ba_{0.9}CuO_{1.93}\cdot(CO_2)_x$ and $Ba_{0.9}CuO_{1.86}\cdot(CO_2)_x$ were studied and the structures were found to differ in terms of the occupancies of two crystallographic positions of oxygen. This conclusion correlates with thermogravimetric data obtained for the same samples in an argon atmosphere since upon heating, oxygen evolution from the fully oxygenated sample was found to occur in two distinct steps.

Interest in mixed-valent transition metal oxides is constantly growing owing to various potential applications based on their electrical, magnetic and superconducting properties, ionic conductivity, catalytic activity, *etc.* Control over the metal valence is most easily achieved in structures allowing oxygen non-stoichiometry. In terms of the tunability of the metal valance, cuprates are among the most flexible transition metal oxides owing to many possible oxidation states and coordination polyhedra of copper. In some cuprate phases the oxygen content and thereby the valence of copper can be altered in distinct steps only, while in others continuous tuning is possible. Among the various mixed-valent cuprate phases, '$BaCuO_{2+\delta}$' shows the most interesting behaviour. The oxygen stoichiometry can be tuned continuously in the lower oxygen concentration range, whereas the oxygen release behaviour is stepwise at higher oxygen contents. This was shown in our previous paper[1] by systematic oxidation/reduction experiments carried out by means of thermogravimetric (TG) analysis. Owing to the possibility of obtaining the '$BaCuO_{2+\delta}$' phase with different oxygen contents it has been successfully utilized as a precursor material for high-pressure synthesis of superconducting cuprates with *in situ*-controlled hole-doping levels.[2,3] Chemical and structural studies on the stoichiometry of the '$BaCuO_{2+\delta}$' phase have revealed, however, not only oxygen non-stoichiometry but also a barium deficiency of *ca.* 10 mol%[1,4–8] and a possibility of carbon contamination.[7,8]

The non-stoichiometry in '$BaCuO_{2+\delta}$' is related to the complexity of its structure. The basic structure of '$BaCuO_{2+\delta}$' was solved for the first time from a single crystal study by Kipka and Müller-Buschbaum[9] in 1977. The structure was described with the space group *Im*3*m* and a lattice constant of *ca.* 18.27 Å. In the cubic unit cell containing 90 formula units, copper ions occupy several different sites in Cu_6O_{12} rings and 26-faced $Cu_{18}O_{24}$ clusters. Later, it was suggested by Paulus *et al.*[4] that the structure of '$BaCuO_{2+\delta}$' is even more complicated than initially believed, consisting of fully and partially occupied parts. The stoichiometry of $Ba_{0.92}Cu_{1.06}O_{2.28}$ as calculated from the refined structure indicates large deviations from the ideal composition in terms of both oxygen content and cation stoichiometry. According to Paulus *et al.*[4] the partially occupied part with two alternate partially filled copper–oxygen clusters without barium atoms fills the space between the structural units of the fully occupied part. The '$BaCuO_{2+\delta}$' structure was also reinvestigated by Aranda and Attfield[7] who performed a simultaneous X-ray and neutron powder diffraction refinement to solve the uncertainties in the partially occupied part of the structure. The carbonate group CO_3^{2-} was found to be an integral part of the structure as for analogous nickel and palladium compounds.[10,11] Furthermore, Skolis and Kovba[8] concluded that presence of carbonate in the synthesis is required to obtain the '$BaCuO_{2+\delta}$' phase. On the other hand, Wong-Ng and Cook[6] claimed that they obtained a $Ba_{0.89}CuO_{2+\delta}$ sample under carbonate-free conditions. Also the structure refinement from powder X-ray diffraction data by Guskos *et al.*[12] is based on a carbonate-free model.

The aim of the present study was to establish the structural changes associated with the changes in the oxygen stoichiometry in the $Ba_{1-y}CuO_{2+\delta}\cdot(CO_2)_x$ system ($y \approx 0.1$).[1] Both X-ray (XRD) and neutron (NPD) powder diffraction techniques were utilized for the structure refinements. Three samples with different oxygen stoichiometries, *i.e.* $Ba_{0.9}CuO_{2.02}\cdot(CO_2)_x$, $Ba_{0.9}CuO_{1.93}\cdot(CO_2)_x$ and $Ba_{0.9}CuO_{1.86}\cdot(CO_2)_x$, were investigated. The refined structural changes were correlated to the oxygen-evolution characteristics observed for the oxygenated $Ba_{0.9}CuO_{2.02}\cdot(CO_2)_x$ phase in reduction experiments carried out in a thermobalance under an argon atmosphere.[1] The possible presence of carbonate in the structure was considered as well.

Experimental

Three $Ba_{0.9}CuO_{2+\delta}\cdot(CO_2)_x$ samples were prepared by the solid state reaction technique from nominal amounts (in terms of Ba and Cu) of BaO_2 and CuO powders. The barium content of the BaO_2 powder was checked prior to use by complexometric titration with EDTA. Synthesis carried out under flowing oxygen gas (99.5%) at 850 °C for 40 h with a subsequent slow cooling to room temperature resulted in single-phase material.

Table 1 The formulae obtained for the $Ba_{0.9}CuO_{2+\delta}\cdot(CO_2)_x$ samples by chemical analysis and structure refinement

Sample	Formula (chem. analysis)	Formula (structure refinement)
Oxygenated	$Ba_{0.9}CuO_{2.02}\cdot(CO_2)_{0.08}$	$Ba_{0.94}CuO_{1.94}\cdot(CO_2)_{0.125}$
Argon annealed ($T = 500$ °C)	$Ba_{0.9}CuO_{1.93}\cdot(CO_2)_{0.07}$	$Ba_{0.94}CuO_{1.82}\cdot(CO_2)_{0.118}$
Argon annealed ($T = 700$ °C)	$Ba_{0.9}CuO_{1.86}\cdot(CO_2)_{0.07}$	$Ba_{0.94}CuO_{1.79}\cdot(CO_2)_{0.111}$

Two reduced $Ba_{0.9}CuO_{2+\delta}\cdot(CO_2)_x$ samples were obtained from the as-'oxygen atmosphere'-synthesized, *i.e.* oxygenated, material by annealing in flowing argon gas (99.9%) for 15 h at 500 and 700 °C. The oxygen stoichiometries of the three samples were established by iodometric titrations and further confirmed by coulometric titration experiments. Details of the chemical analysis have been described earlier.[1]

Within the available analysis techniques it was not possible to determine the exact carbon content in the samples. However, an estimation for the amount of carbonate in the samples could be obtained from thermogravimetric H_2 reduction experiments. In the H_2/TG reduction the sample powders were reduced in a thermobalance by heating to 1000 °C with a heating rate of 2 °C min^{-1} in a 5% H_2–95% Ar atmosphere. Under these conditions copper is reduced to the metallic state while barium is maintained in an oxide form. The possible carbon in the sample is liberated as carbon dioxide. If the sample does not contain carbonate, the H_2/TG reduction would reveal the oxygen content of the sample. On the other hand, if the sample contains carbonate the observed weight loss in the H_2/TG reduction is the sum of contributions from both the excess oxygen and the amount of carbonate, as shown in eqn. (1). From the titration and H_2/TG reduction results, the oxygen and carbonate contents can be iterated in a self-consistent way.

$$Ba_{0.9}CuO_{2+\delta}\cdot(CO_2)_x + (1.1+\delta)H_2 \rightarrow 0.9BaO + Cu + (1.1+\delta)H_2O\uparrow + xCO_2\uparrow \quad (1)$$

The oxygen-evolution *versus* temperature characteristics of the as-synthesized $Ba_{0.9}CuO_{2+\delta}\cdot(CO_2)_x$ material was also followed

Table 2 The NPD refinement results for $Ba_{0.9}CuO_{2.02}\cdot(CO_2)_x$ (upper; $R_p = 3.27\%$, $R_{wp} = 4.27\%$, $\chi^2 = 3.81$, $R_f = 4.24\%$), $Ba_{0.9}CuO_{1.93}\cdot(CO_2)_x$ (middle; $R_p = 3.37\%$, $R_{wp} = 4.54\%$, $\chi^2 = 4.35$, $R_f = 5.09\%$) and $Ba_{0.9}CuO_{1.86}\cdot(CO_2)_x$ (lowest; $R_p = 2.22\%$, $R_{wp} = 2.90\%$, $\chi^2 = 2.44$, $R_f = 4.89\%$)

Atom	Position	*x*	*y*	*z*	*n*	*B*/Å^2
Ba(1)	48j	0	0.1486(5)	0.3174(4)	1	0.9(2)
		0	0.1490(5)	0.3150(4)	1	0.7(2)
		0	0.1486(6)	0.3136(6)	1	1.1(3)
Ba(2)	24h	0.3670(5)	0.3670(5)	0	1	1.4(3)
		0.3623(5)	0.3623(5)	0	1	1.6(3)
		0.3633(8)	0.3633(8)	0	1	2.6(4)
Ba(3)	16f	0.1768(5)	0.1768(5)	0.1768(5)	1	1.5(4)
		0.1784(6)	0.1784(6)	0.1784(6)	1	2.7(4)
		0.1781(7)	0.1781(7)	0.1781(7)	1	2.1(5)
Cu(1)	48i	0.1490(11)	0.25	0.6496(10)	1	1.8(2)
		0.1497(25)	0.25	0.6489(27)	1	2.2(3)
		0.1449(11)	0.25	0.6537(11)	1	2.1(4)
Cu(2)	24h	0.1258(3)	0	0.1258(3)	1	0.9(3)
		0.1254(3)	0	0.1254(3)	1	0.6(2)
		0.1249(5)	0	0.1249(4)	1	0.2(2)
Cu(3)	12e	0.2065(6)	0	0	1	1.3(4)
		0.2063(6)	0	0	1	1.5(3)
		0.2074(9)	0	0	1	2.1(5)
Cu(4)	12e	0	0.5610(9)	0	0.79	2.6(4)
		0	0.5624(12)	0	0.79	5.4(3)
		0	0.5627(15)	0	0.79	5.0(4)
C	12d	0.25	0.5	0	1	1.2(3)
		0.25	0.5	0	0.94(2)	2.7(4)
		0.25	0.5	0	0.89(3)	3.8(4)
O(1)	48k	0.0741(3)	0.1868(4)	0.0741(3)	1	0.4(2)
		0.0740(3)	0.1866(4)	0.0740(3)	1	0.3(1)
		0.0739(4)	0.1866(4)	0.0739(4)	1	0.3(2)
O(2)	48k	0.6451(3)	0.6451(3)	0.8397(5)	1	1.4(2)
		0.6425(4)	0.6425(4)	0.8449(5)	1	2.0(2)
		0.6419(5)	0.6419(5)	0.8457(7)	1	3.1(3)
O(3)	48k	0.4130(4)	0.2323(3)	0.2323(3)	1	0.5(2)
		0.4134(4)	0.2339(4)	0.2339(3)	1	0.7(2)
		0.4135(5)	0.2354(4)	0.2354(4)	1	0.4(2)
O(4)	12e	0	0.6627(10)	0	1	2.5(4)
		0	0.6627(9)	0	1	2.1(4)
		0	0.6638(14)	0	1	3.4(6)
O(5)	24g	0.0924(10)	0.5	0	0.53(2)	1.50
		0.0930(14)	0.5	0	0.36(3)	1.50
		0.0935(19)	0.5	0	0.37(3)	1.50
O(6)	48j	0	0.2209(13)	0.4391(12)	0.36(3)	1.50
		0	0.2148(14)	0.4440(12)	0.39(3)	1.50
		0	0.2165(18)	0.4439(17)	0.34(3)	1.50
O(7)	48i	0.4347(6)	0.0653(6)	0.25	0.40(1)	1.50
		0.4369(10)	0.0631(10)	0.25	0.28(1)	1.50
		0.4384(10)	0.0616(10)	0.25	0.26(2)	1.50

Space group *Im*3*m*, lattice parameters: $a = b = c = 18.2597$ Å for the oxygenated samples, $a = 18.2334$ Å and $a = 18.2394$ Å for the samples annealed in argon at 500 and 700 °C, respectively.

in situ with a TG measurement carried out at a slow heating rate of 2 °C min^{-1} in flowing argon in a Perkin Elmer System 7 thermobalance. The mass of the sample in all TG experiments was around 35 mg.

Powder X-ray diffraction data were collected with a Philips PW1830 powder diffractometer using Cu-Kα radiation [$K\alpha_1 = 1.54060$ Å and $K\alpha_2 = 1.54439$ Å, $I(K\alpha_2/K\alpha_1) = 0.5$]. The measurements were carried out over the 2θ range 10.010–69.990° with a step size of 0.020°. The measurement time for each step was 20 s. Neutron diffraction experiments were carried out at the R2 reactor in Studsvik, Sweden. A neutron powder diffractometer consisting of a double Cu(220) monochromator system ($\lambda = 1.470$ Å) and 35 ^{3}He detectors spaced 4.00° apart from each other, was used for the precise structure determination by scanning in steps of 0.08° over the 2θ range 4.00–139.92°. The powder samples (*ca.* 3.0 g) were placed in vanadium sample holders with a diameter of 6 mm, and the data were collected at 298 K. The neutron flux at the sample was *ca.* 10^6 cm^{-2} s^{-1}. The structure refinements were made from both XRD and NPD data by the Rietveld refinement technique using the refinement program FULLPROF.[13] The scattering lengths for neutrons are, Ba: 0.507×10^{-12} cm, Cu: 0.7718×10^{-12} cm, C: 0.6646×10^{-12} cm and O: 0.5805×10^{-12} cm.[13]

Results

Table 1 summarizes the results obtained from the iodometric titration and H_2/TG reduction for the oxygen stoichiometry and carbonate content. The carbonate content x was found to be constant in all three $Ba_{0.9}CuO_{2+\delta}\cdot(CO_2)_x$ ($x \approx 0.07 \pm 0.02$) samples with the oxygen content $2+\delta$ ranging from 1.86 ± 0.01 to 2.02 ± 0.01.

The starting model for the Rietveld refinements of the $Ba_{0.9}CuO_{2+\delta}\cdot(CO_2)_x$ structure was extracted from literature data.[4,5,7,9] The cation positions were first refined using the X-ray diffraction data. The complex structure with various partially occupied oxygen positions was then refined from the NPD data. Since the goal of the present study was to determine small structural changes with decreasing oxygen content special care was taken to refine the data of all three samples in a consistent way. From the three samples, the as-synthesized, oxygenated $Ba_{0.9}CuO_{2.02}\cdot(CO_2)_x$ sample was studied first in order to determine the oxygen positions as accurately as possible.

Among the cation sites, full occupancy of three barium sites, *i.e.* Ba(1), Ba(2) and Ba(3), and three copper sites, *i.e.* Cu(1), Cu(2) and Cu(3), was confirmed. The 12e site, *i.e.* Cu(4), was found to be occupied by copper to an extent of 79% (Table 2) in accordance with previous studies. Only the assignment of the 12d cation site remained controversial. This is the site at which Aranda and Attfield[7] introduced carbon into their structure model. The present refinement from the X-ray diffraction data led to full occupancy of the site by copper. However, the cation–oxygen bond lengths calculated for this site from the neutron diffraction data are definitely too short to support this assumption. In preliminary neutron diffraction refinements the structure was therefore modelled and refined for both the possible cation constituents separately, but no clear conclusion on the site assignment could be made based on the obtained R-values. For the final refinements, carbon was chosen at the 12d site. Note that the purpose of the present study was to determine the changes in the occupancies of the different oxygen sites. Fortunately for this goal, the assignment of the 12d site was found not to have any significant effect.

The present notation system for the oxygen atoms O(1)–O(3) was adopted from previous studies.[4,5,7,9,12] The notation of the other oxygen atoms is provided in Table 2 and will be explained later. Owing to the low occupancy of oxygen sites in the partially occupied part the thermal parameters of those sites were fixed at 2.0. According to Paulus *et al.*[4,5] the partially occupied part consists of several partially occupied oxygen positions (atoms indicated by label A) around partially occupied copper positions Cu(4) and Cu(5), *i.e.* the 12e and 12d sites. In the present study, the oxygen atom O(5) [A(6)] at the 24g site was found to improve the fit significantly. Oxygen at the O(6) [A(8)] site was also evident, and the fitting was further improved by taking the O(7) [A(9)] oxygen site into consideration. The other oxygen sites proposed by Paulus *et al.*[4,5] were also introduced into the structure model, but since the fit was not improved with any of these oxygen atoms, they were omitted in the final refinements.

The structures of the argon-annealed samples $Ba_{0.9}CuO_{1.93}\cdot(CO_2)_x$ and $Ba_{0.9}CuO_{1.86}\cdot(CO_2)_x$ were obtained using the refinement result of the oxygenated sample as a starting point and following a similar procedure of refinement. The agreement factors obtained for the refinements of all three samples are excellent indicating that the refined structural model describes the structures very well. The results of the refinements are summarized in Table 2.

It has been proposed in several papers[14–16] that the

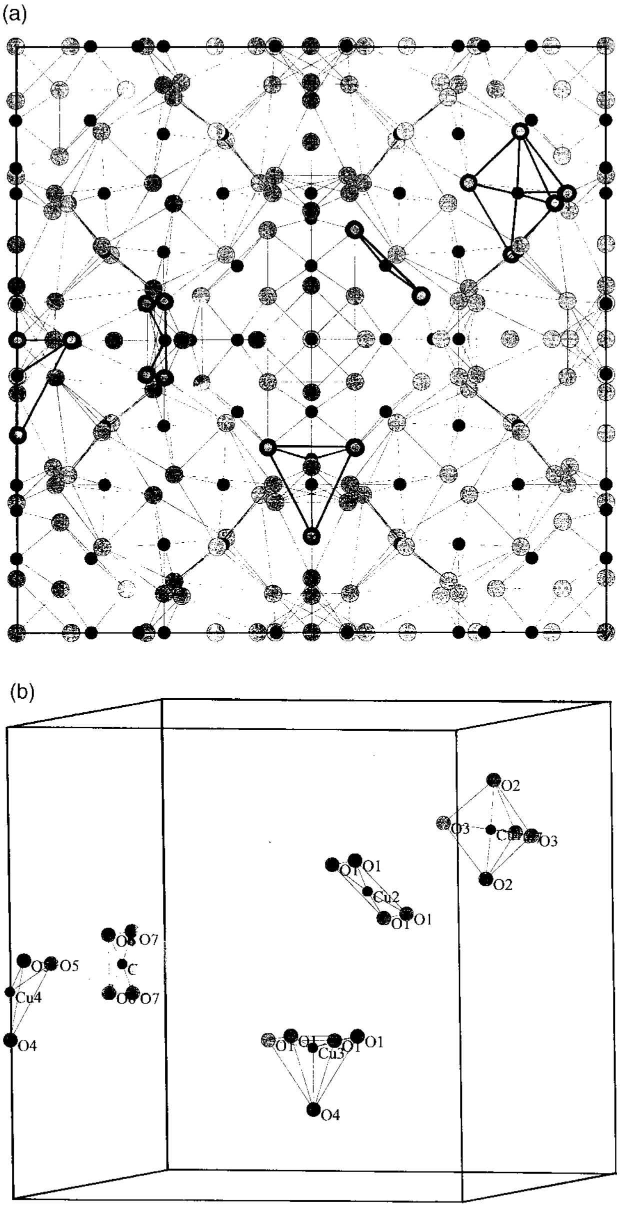

Fig. 1 (a) Copper/carbon–oxygen network and (b) different copper/carbon–oxygen coordination polyhedra in the structure of $Ba_{0.9}CuO_{2+\delta}\cdot(CO_2)_x$.

removable oxygen atoms would fill the O(6) site which, however, is not supported by the present refinement results, since the occupancy of the O(6) site was found to be the same for all three samples. On the other hand, the occupancy of the O(5) oxygen site was found to first decrease with decreasing overall oxygen content, *i.e.* from *ca.* 53 to 36% when the oxygen content decreased from $2+\delta=2.02$ to 1.93. Also the occupancy of the O(7) site was lower in the partially reduced $Ba_{0.9}CuO_{1.93}{\cdot}(CO_2)_x$ sample (28%) than in the oxygenated $Ba_{0.9}CuO_{2.02}{\cdot}(CO_2)_x$ sample (40%). With a further decrease in the oxygen content to $2+\delta=1.86$ the occupancy of the O(5) site remained unchanged and oxygen was liberated from the O(7) site only.

The formulae of the three samples as calculated from the refined atomic occupancies are given in Table 1 together with the results of chemical analysis. Even though the chemical analysis suggested an essentially constant carbonate content in all three samples, the occupancy at the 12d site seemed to decrease slightly upon annealing in argon according to the structural data.

Discussion

The copper–oxygen network of the structure [Fig. 1(a)] is comprised of fully occupied Cu_6O_{12} rings with Cu(1), and $Cu_{18}O_{24}$ clusters with Cu(2) and Cu(3) atoms. The Cu(4) and C atoms are located between the clusters in the partially occupied part of the structure. The Cu(4) atoms are connected to Cu(3) by O(4) atoms, while C in the carbonate group is linked *via* O(7) atoms to the Cu(1) atoms in the Cu_6O_{12} rings. The removable O(5) atoms form a square-planar coordination sphere around Cu(4) as shown in Fig. 1(b).

The occupation of the 12d site has been a topic of debate. This is the site that Aranda and Attfield[7] proposed to be occupied by carbon, the reasoning being mainly based on the short cation–oxygen bond lengths (≈ 1.2 Å). If the site were fully occupied by carbon the carbonate content per formula unit would be $x=0.125$. This value is almost twice as high as the estimate obtained in the present study from the chemical analysis. On the other hand, not only in this study but also in the study of Guskos *et al.*[12] the refinements based on the X-ray diffraction technique, which should be quite sensitive in distinguishing carbon and copper, suggested copper at this site. It is also possible that the synthesis conditions may have some effect on the composition of the '$BaCuO_{2+\delta}$' phase. Owing to the uncertainty concerning the 12d site, special attention was paid to carefully checking that the changes in the occupancies of the oxygen sites were independent of the 12d site occupation.

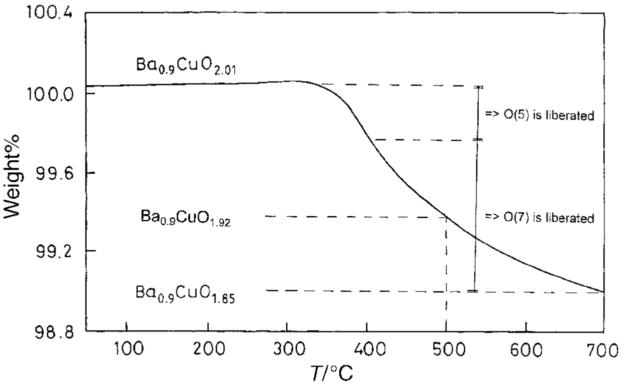

Fig. 2 TG curve for the reduction of $Ba_{0.9}CuO_{2.02}{\cdot}(CO_2)_x$ in an argon atmosphere up to 700 °C. The synthesized samples are indicated.

According to the present structure refinements, the O(5) atoms are most easily released from the $Ba_{1-y}CuO_{2+\delta}{\cdot}(CO_2)_x$ structure upon reduction. In the oxygenated sample the occupancy of the O(5) site is *ca.* 53% while in the reduced samples it is *ca.* 36%. This difference corresponds to a weight change of 0.29%, which is very close to the value observed reproducibly in TG experiments performed in an argon atmosphere at 330–370 °C (Fig. 2). Previously[1] this oxygen

Table 3 Bond lengths (Å) calculated from the NPD refinement results for the $Ba_{0.9}CuO_{2+\delta}{\cdot}(CO_2)_x$ samples

	$Ba_{0.9}CuO_{2.02}{\cdot}(CO_2)_x$	$Ba_{0.9}CuO_{1.93}{\cdot}(CO_2)_x$	$Ba_{0.9}CuO_{1.86}{\cdot}(CO_2)_x$
Ba(1)–O(1)	3.0605	3.0279	3.0055
Ba(1)–O(2)	2.6804	2.6582	2.6639
Ba(1)–O(3)	2.8422	2.8007	2.7849
Ba(1)–O(4)	2.7371	2.7476	2.7415
Ba(1)–O(6)	2.5853	2.6412	2.6815
Ba(1)–O(7)	3.0725	3.1077	3.1416
Ba(2)–O(2)	2.9440	2.8309	2.8281
Ba(2)–O(3)	3.0176	2.9402	2.9832
Ba(2)–O(5)	2.5384	2.6397	2.6140
Ba(2)–O(6)	3.1159	3.0534	3.0628
Ba(2)–O(7)	2.7413	2.7142	2.7222
Ba(3)–O(1)	2.6584	2.6949	2.6922
Ba(3)–O(2)	3.0856	3.1734	3.1823
Ba(3)–O(3)	2.8633	2.8142	2.7997
Cu(1)–O(2)	1.9343	1.9672	1.9804
Cu(1)–O(3)	1.9229	1.9530	1.8514
Cu(1)–O(7)	2.1692	2.2219	2.2653
Cu(2)–O(1)	1.9904	1.9861	1.9875
Cu(3)–O(1)	1.9457	1.9423	1.9447
Cu(3)–O(4)	2.3893	2.3897	2.3487
Cu(4)–O(4)	1.8576	1.8297	1.8453
Cu(4)–O(5)	2.0215	2.0442	2.0554
C–O(6)	1.2324	1.2058	1.1910
C–O(7)	1.6860	1.6273	1.5882

evolution was shown to occur in a single step. After this rather sharp reduction step, the slope of the TG reduction curve changes when the O(7) atoms start to be removed from the structure, suggesting that the occupancy of the O(7) site can be tuned in a continuous way (Fig. 2). The decrease in the occupancy of the O(7) site from 40% [$Ba_{0.9}CuO_{2.02}\cdot(CO_2)_x$] to 26% [$Ba_{0.9}CuO_{1.86}\cdot(CO_2)_x$] when the oxygenated sample was annealed in argon to 700 °C corresponds to a weight change of 0.50%, in reasonable agreement with the TG data (Fig. 2). Note that Guskos *et al.*[12] found the O(7) site to be vacant in their sample reduced under He flow at 900 °C.

All the bond lengths obtained from the refinements for the coordination polyhedra of the barium and copper atoms can be considered reasonable (Table 3). The loss of O(5) atoms around the Cu(4) site is reflected in the valence of Cu(4) only. Bond valence sum[17] calculations show the Cu(4) valence decreases from $+2.28$ to $+1.74$ and further to $+1.71$ when the oxygen content $2+\delta$ changes from 2.02 to 1.93 and 1.86, respectively. It should also be noted that the obtained cation–oxygen bond lengths around the 12d site would result in quite a low valence value of *ca.* $+3$ for carbon.

Conclusions

On the basis of Rietveld refinement of both neutron and X-ray powder diffraction data, occupancies of two oxygen sites, O(5) and O(7), in the partially occupied part of the structure were found to be changed when the oxygen content of the $Ba_{0.9}CuO_{2+\delta}\cdot(CO_2)_x$ phase was varied. Observation of two distinct onset temperatures for the oxygen evolution in the TG reduction experiments suggested that the bonding strengths of these two oxygen sites are different. Since the assignment of the 12d cation site could not be completely established some uncertainty concerning the surrounding oxygen sites, including the O(7) site, still remains.

The present work explains the origin of the capability of '$BaCuO_{2+\delta}$' to act as an oxygen source, *e.g.* in the high-pressure synthesis of superconducting cuprates. Owing to the removability of O(5) atoms, the Cu(4) site cations possess the required oxidizing power.

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References

1 K. Peitola, K. Fujinami, M. Karppinen, H. Yamauchi and L. Niinistö, *J. Mater. Chem.*, 1999, **9**, 465.

2 K. Fujinami, T. Ito, H. Suematsu, K. Matsuura, M. Karppinen and H. Yamauchi, *Phys. Rev. B*, 1997, **56**, 14790.

3 T. Ito, H. Suematsu, M. Karppinen and H. Yamauchi, *Physica C*, 1998, **308**, 198.

4 E. F. Paulus, G. Miehe, H. Fuess, I. Yehia and U. Löchner, *J. Solid State Chem.*, 1991, **90**, 17.

5 E. F. Paulus, G. Wltschek and H. Fuess, *Z. Kristallogr*, 1994, **209**, 586.

6 W. Wong-Ng and L. P. Cook, *Physica B*, 1996, **273**, 135.

7 M. A. G. Aranda and J. P. Attfeld, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 454.

8 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.

9 R. Kipka and H. Müller-Buschbaum, *Z. Naturforsch., Teil B*, 1997, **32**, 121.

10 R. Gottschall and R. Schöllhorn, *Solid State Ionics*, 1993, **59**, 93.

11 R. J. Crooks and M. T. Weller, *J. Solid State Chem.*, 1997, **128**, 220.

12 N. Guskos, V. Likodimos, C. A. Londos, V. Psycharis, C. Mitros, A. Koufoudakis, H. Gamari-Seale, W. Windsch and H. Metz, *J. Solid State Chem.*, 1995, **119**, 50.

13 J. Rodriguez-Carvajal, in *Collected Abstracts of Power Diffraction Meeting*, Toulouse, France, July 1990, p. 127.

14 H. N. Migeon, F. Jeannot, M. Zanne and J. Aubry, *Rev. Chim. Miner.*, 1976, **13**, 440.

15 H. N. Migeon, M. Zanne, F. Jeannot and C. Gleitzer, *Rev. Chim. Miner.*, 1977, **14**, 498.

16 M. T. Weller and D. R. Lines, *J. Solid State Chem.*, 1989, **82**, 21.

17 I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B.*, 1985, **41**, 244.

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