Defect Chemistry of “$BaCuO_2$” I. Oxygen Non-Stoichiometry, Cation Molecularity and X-ray Diffraction Determinations

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“$BaCuO_2$” is the key intermediate in the synthesis of the $Ba_2YCu_3O_{7-\delta}$ superconductor. Its very complex crystal structure is able to accommodate a large change in oxygen content.

Oxygen non-stoichiometry of “$BaCuO_2$” materials with 1:1 and 88:90 (Ba:Cu) molecularity has been investigated by polythermal X-ray powder diffraction coupled with isobaric-isothermal gravimetry determinations under different temperature and oxygen partial pressure conditions [$300 \leq T \leq 820\,°C$, $1 \geq P(O_2) \geq 3 \cdot 10^{-3}$ atm].

The 1:1 composition does not give well reproducible results, thus suggesting its polyphasic nature, at least in part of the investigated range. The results for the $88{:}90 \cong 0.98$ (Ba:Cu) composition are well reproducible and show that the material is single phase. $Ba_{0.98}CuO_{1.98+\delta}$ is oxygen over-stoichiometric in the whole investigated [T, $P(O_2)$] range, with a maximum value $\delta \sim 0.21$. A Rietveld X-ray profile fitting is in agreement with previous single-crystal data. The trend of δ vs. $P(O_2)$ is consistent with the presence of oxygen interstitial defects on (possibly different) crystallographic sites.

Key words: $BaCuO_2$, Superconductors, Oxygen non-stoichiometry.

1. Introduction

The binary oxide usually written as $BaCuO_2$ is a well known precursor of the $YBa_2Cu_3O_{7-\delta}$ superconductor. Previous works by our group have shown that this phase plays a critical role in the solid state synthesis of $YBa_2Cu_3O_{7-\delta}$ [1], and that its formation follows different and complex mechanisms when performed under different external [T, $P(O_2)$] conditions or from different precursors [2]. This is due to a mix of thermodynamic and kinetic factors, and its complete understanding requires a (still lacking) knowledge of the defect chemistry of the phase.

After the first work by Arjomand and Machin [3], “$BaCuO_2$” has been investigated as to space group symmetry [4], crystal structure determination from single crystal and powder Rietveld methods [5–10], oxygen non-stoichiometry and cation molecularity [9–15], thermodynamic data [15, 16], Raman spectroscopy [17], electrical conductivity [4, 11], thermopower [4, 11], and magnetic and ferroelectric behavior [4, 11, 18]. Crystallography and crystal chemistry of the various compounds in the whole Ba, Cu/O system have been recently reviewed by Wong-Ng and Cook [19].

These investigations show a complex behavior for what concerns, for instance, crystal structure, formula unit and molecularity (Ba/Cu ratio), and nature and amount of (oxygen) non-stoichiometry. In some cases, conflicting results have been reported. Many fundamental aspects of this phase still remain unclear. In particular, the uncertainty concerns the nature of predominant point (atomic) and electronic defects, as well as the influence of temperature and external oxygen atmosphere on the amount of these defects.

We here start an investigation of “$BaCuO_2$” using different experimental techniques. It is the aim of this investigation both to give a contribution to the understanding of those yet unclear aspects, and to face the defect chemistry and defect-related properties of the phase. The present part I reports direct oxygen non-stoichiometry determinations with a gravimetric method coupled with X-ray powder diffraction determinations under a broad range of temperature and oxygen partial pressure conditions. Part II will deal with electrical conductivity and thermopower measurements.

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2. Experimental

2.1. Materials

The "$BaCuO_2$" materials with different Ba:Cu molecularities were synthesized by solid state reaction of BaO_2 and CuO (both Fluka *puriss.*). Appropriate amounts of the reagent powders were weighted, mixed, pressed into pellets, and allowed to react in pure oxygen at 1 atm pressure and 830±5 °C for 24 hours. After cooling, regrinding and repelletization, the samples were heated again to 900±5 °C for one hundred hours under pure oxygen.

The samples for diffractometric determinations were prepared in this way using an external furnace, then placed in the polythermal chamber of the diffractometer and submitted to a further heating cycle to 900 °C under pure oxygen before setting the temperature and oxygen partial pressure of any pattern collection.

A different procedure was employed for the gravimetric determinations. Indeed, a reliable measurement of oxygen non-stoichiometry in "$BaCuO_2$" is difficult for several reasons. We may remind here that: a) the phase is highly reactive with crucible materials and with moisture or carbon dioxide, b) the Ba, Cu/O system shows many different phases [19], so that many heterogeneous equilibria should be expected under different (and go yet well known) T, $P(O_2)$ conditions, c) the parent materials themselves undergo various heterogeneous equilibria (for instance: $Cu/Cu_2O/CuO$, $BaO/BaO_2,\ldots$), d) in some cases the formation reaction is very sluggish and even does not go to complete conversion [1]. Some of these processes can occur unnoticed, most notably during the non-stoichiometry determination by gravimetry. Therefore, the synthesis of "$BaCuO_2$" samples for the gravimetric determinations was directly performed *in situ*. To this purpose, we directly used pressed pellets of the powder mixture of the reagents. Before starting the non-stoichiometry measurements, each sample was submitted to a heating cycle similar to that described above, but for the intermediate cooling step with grinding and repelletization.

A flux of pure oxygen or certified oxygen-in-argon mixtures at one atm total pressure was used to set the environmental atmosphere of the gravimetric and diffractometric determinations.

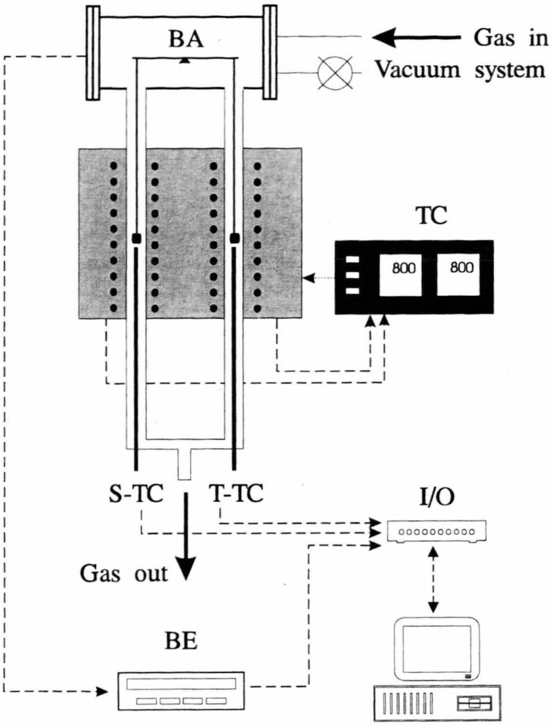

Fig. 1. Apparatus for gravimetric determination of Oxygen non-stoichiometry: BA: Cahn Rg Automatic balance, BE: electronics of the balance, TC: temperature controller, S-TC: thermocouple for sample, T-TC: thermocouple for tare, I/O: Input/output processor.

2.2. Instruments and Methods

The oxygen stoichiometry was measured with a gravimetric method under isothermal-isobaric conditions. The homemade apparatus (see Fig. 1) was built around a Cahn RG Automatic balance having a stated sensitivity of 10^{-7} g and a maximum load of 1 g. In designing the apparatus, due care was taken to keep the symmetric arrangement of the balance. In particular, the crucibles for sample and tare drop from two equally spaced loops on the balance arms. Also, the two quartz tubes enclosing the crucible wires were symmetrically fastened to the stainless steel container of the balance (on top) and to a Pyrex connection with a common outlet (on bottom). Therefore, the gas flux used to set the operation atmosphere was symmetrically divided between sample and tare. Finally, heating was provided by a twin furnace operated by two control/power units in a master/slave configuration and driven by two (pilot) thermocouples equally placed with respect to each winding of the furnace. The apparatus was also connected to some auxiliary devices for controlling and measuring the gas flow, and to vacuum pumps and manometers for the preliminary outgassing operations. Following a programmable measurement cycle, a µMAC (Analog Devices) Input/Output (I/O) processor collected analog inputs from the electronics of the balance, from the (measurement) thermocouples, and from any other appropriate transducer, and sent upon request all these data to a personal computer through a serial interface. A first homemade programme was used to set the measurement cycle, to dialog with the I/O processor, to store the acquired data on disk, and to graphically display on-line the time evolution of process variables. Another programme was used for offline analysis of the stored data.

The experimental procedure was as follows. For each sample, there is a *starting* run, then a series of *measurement* runs, and a *final* run. Moreover, a number of *control* runs was done after the *starting* run, between the *measurement* runs, and before the *final* run. Goal of the *starting* run (under pure oxygen) was to accomplish the synthesis of "$BaCuO_2$", as described in the previous section, and to verify its completeness. Goal of the *final* run was to give the absolute value of oxygen content by measuring the weight loss corresponding to the chemical reduction under a 5% hydrogen-in-argon mixture. Each *measurement* run corresponded to a particular flux gas, *i.e.* a particular $P(O_2)$, and several different temperatures: at each $[T, P(O_2)]$ couple, the sample weight vs. time plot was recorded until a stable plateau was seen. Care was taken to select a temperature sequence, within each run, to reach the same $[T, P(O_2)]$ conditions both from lower and from higher temperatures. At the end of each *measurement* run, the weight of the sample at selected temperatures was obtained from a least squares fit of the raw (weight vs. T) data. Finally, during each *control* run a weight measurement under a fixed set of $[T, P(O_2)]$ conditions was made to assess the reproducibility of the whole procedure, and to provide a single reference state for connecting all relative and absolute determinations.

X-ray powder diffraction (XRPD) patterns were taken with a Philips 1710 diffractometer using a copper anode ($\lambda = 0.15418$ nm) operated at 40 kV and 35 mA, graphite monochromator on the diffracted beam, proportional counter, and a homemade polythermal attachment [20]. The lattice dimensions were obtained by minimizing the squared differences between calculated and experimental Q values ($Q_i = 4\sin^2\theta_i/\lambda_i^2$, θ_i = diffraction angle) with weights proportional to $[\sin(2\theta_i)]^{-2}$. Due allowance was made for systematic errors by inserting an appropriate term into the linearized fitting model [21]. For more reproducible results, the same set of XRPD lines were used for all patterns.

For the Rietveld refinements [22, 23] of the crystal structure, we used version 3.5 of the WYRIET programme [24].

3. Results

3.1. Crystal Structure, Unit Cell and Cation Molecularity

At least three ternary compouds have been reported in the Ba, Cu/O system around the 1:1 (Ba:Cu) composition [19]. The phase under investigation here corresponds to the lowest oxygen content, is easily identified from its cubic diffraction pattern, and is usually written for short as "$BaCuO_2$". To our knowledge, it was first discussed in a full paper by Arjomand and Machin [3] during a systematic work on copper-based ternary (two-cations) oxides. The same Authors also gave an unindexed list of poweder X-ray diffraction lines and a preliminary characterization of its magnetic properties. According to the electron diffraction determinations of Migeon et al. [4], the crystal structure belongs to one of the space groups $Im3m$, $I\bar{4}3m$ or $I432$, the cubic unit cell is ~ 1.826 nm wide, and contains ~ 90 ($BaCuO_2$) formula units. The following papers were in agreement with these data as well as with the indexed diffraction pattern given by the latter Authors.

A full structure determination was first reported by Kipka and Müller-Buschbaum [5] from single-crystral X-ray diffraction data. These Authors described a (previously unknown) crystal structure belonging to the space group $Im3m$, with 360 atoms in the cubic unit cell. Each chemical species occupies several (up to six) different sets of crystallographically equivalent positions. Exact $BaCuO_2$ stoichiometry requires fractional occupancies (1/4 and 1/2) for one oxygen site and one copper site. One of the Ba^{2+} positions has the extraordinary coordination number of 24. It was later found that, under appropriate conditions, also "$BaNiO_2$" crystallizes in this crystal structure [25].

Weller and Lines [6, 26] later re-investigated the crystal structure using neutron powder diffraction, with the main aim of determining more precisely positions and occupancies of the oxygens and their dependence on external conditions. From crystal-chemical arguments, and from the failure of the attempts to refine its temperature factors, they also suggested the removal of the Barium atom at the origin of the cell (the atom with 24-fold coordination according to Kipka and Müller-Buschbaum). Accordingly, the cation molecularity should be $Ba/Cu = 88/90$ (~ 0.98). Later papers by Gutau and Müller-Buschbaum [8], and by Paulus, Fuess et al. [7, 9, 10] confirmed that this position should be removed.

The last Authors used X-ray diffraction on a single crystal coming from $YBa_2Cu_3O_{7-\delta}$ synthesis by a flux method. According to their work, the crystal structure is not very different from that described by Müller-Buschbaum et al. [5, 8] and by Weller and Lines [6, 26], and can be more precisely divided into an ordered and a disordered part. The ordered part is built up [9] of: a) $Cu_{18}O_{24}$ bodies located in the origin and in the center of the cell, b) oxygen-bridged Cu_6O_{12} rings, c) various Ba ions around the Cu-O clusters, and d) fully occupied oxygen positions along the cell axis and in the equivalent position corresponding to cell centering. The disordered part of the structure is more controversial: according to the latest determination [9] it consists of Cu_2O_6 and CuO_4 clusters with incomplete occupancies.

Taking into account these results, it is not unreasonable to infer that, by allowing variable amounts on the "disordered" part, the structure can allow variable degrees both of oxygen stoichiometry [$O/(Ba + Cu)$ ratio] and cation molecularity [Ba/Cu ratio].

Starting from the single crystal results at 193 K from Paulus et al. [9], we made a series of Rietveld refinements of "$BaCuO_2$" samples in equilibrium with different temperature and oxygen pressure conditions but prepared with a *fixed* (88:90) Ba:Cu ratio. This choice is due to the following reasons. Major emphasis is given here to the investigation of oxygen stoichiometry because of its remarkable effect on the solid state reactivity during the synthesis of $YBa_2Cu_3O_y$. The 88/90 cation ratio corresponds to the knowledge of the molecularity of the phase available when this work was started. According to our understanding (see following section), the 88/90 molecularity is indeed within the stability field of the phase, but this does not seem true for the 1:1 molecularity. Finally, interest in the defect chemistry of this phase for the formation mechanisms of oxide superconductors is focused on a Ba:Cu molecularity as close as possible to 1:1.

The general strategy used in the Rietveld refinements can be briefly summarized as follows. (For better clarity, the different sites are hereafter denoted according to Paulus et al. [9]).

a) We first optimized only profile, scale, background, and zero error parameters, and lattice constants. In these preliminary runs, i) we used exactly the atomic coordinates of the above reference and complete occupancies of the "ordered" part [Ba1, Ba2, Ba3, Cu1, Cu2, Cu3, O1, O2, O3, O5]; ii) the overall Cu and O occupancies of the "disordered" part [Cu4, Cu5, O6, O7] were fixed at the values corresponding to the actual cation molecularity and oxygen stoichiometry of our samples (as given by starting composition and gravimetric determinations, respectively); iii) the Cu4/Cu5 and O6/O7 ratios were taken from Paulus et al. [9].
b) Then, we relaxed the atomic positions of the ordered part and the atomic positions and the *relative* occupancies of Cu4 and Cu5, and O6 and O7, but still keeping fixed their overall values.
c) Finally, we removed the constraint about the overall copper content.

Figure 2 shows the final profile fit, and Table 1 reports the results corresponding to steps b) and c) of the

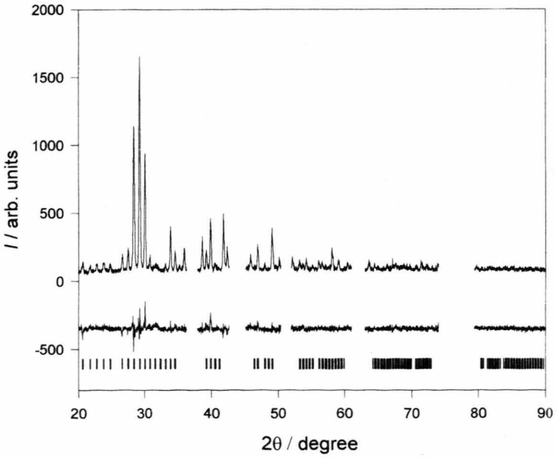

Fig. 2. Rietveld profile fitting of $Ba_{0.98}CuO_{2.14}$ at $T = 571\,°C$ and $P(O_2) = 9.8 \cdot 10^{-3}$ atm. Upper part: experimental profile; middle part: difference (experimental – calculated); lower part: peak positions.

Table 1. Crystal structure data: comparison of the present data (optimization steps b and c) with the results from single crystal work by Paulus et al. [9].

		This work, 571 °C $9.8 \cdot 10^{-3}$ atm O_2										E.F. Paulus et al. ref [9], 193 K			
		step b					step c								
Atoms	Multipl.	x	y	z	B	Occup.	x	y	z	B	Occup.	x	y	z	Occup.
Ba(1)	48	0	0.1497	0.3110	3.076	1	0	0.1497	0.3110	3.076	1	0	0.1520	0.3131	1
Ba(2)	24	0.3638	0.3638	0	4.025	1	0.3638	0.3638	0	4.025	1	0.3619	0.3619	0	1
Ba(3)	16	0.1745	0.1745	0.1745	2.785	1	0.1745	0.1745	0.1745	2.785	1	0.1770	0.1770	0.1770	1
Cu(1)	48	0.6480	1/4	0.1480	2.538	1	0.6480	1/4	0.1480	2.538	1	0.6490	1/4	0.1490	1
Cu(2)	24	0.1316	0	0.1316	7.719	1	0.1316	0	0.1316	7.719	1	0.1248	0	0.1248	1
Cu(3)	12	0.2161	0	0	2.349	1	0.2161	0	0	2.349	1	0.2051	0	0	1
Cu(4)	12	0	0.5432	0	1.322	0.304	0	0.5432	0	6.198	0.417	0	0.5670	0	0.84
Cu(5)	12	1/4	1/2	0	−1.175	0.196	1/4	1/2	0	5.871	0.335	1/4	1/2	0	0.61
O(1)	48	0.0675	0.1910	0.0675	0.241	1	0.0675	0.1910	0.0675	0.242	1	0.0733	0.1864	0.0733	1
O(2)	48	0.6517	0.6517	0.8506	1.396	1	0.6517	0.6517	0.8506	1.958	1	0.6462	0.6462	0.8390	1
O(3)	48	0.3967	0.2223	0.2223	1.276	1	0.3967	0.2223	0.2223	1.276	1	0.4139	0.2329	0.2329	1
O(5)	12	0	0.6563	0	1.422	1	0	0.6563	0	1.422	1	0	0.6655	0	1
O(6)	24	0.0538	1/2	0	3.036	0.534	0.0538	1/2	0	6.334	0.564	0.0765	0.5	0	0.84
O(7)	48	0.4306	0.0694	1/4	4.663	0.504	0.4306	0.0694	1/4	5.013	0.489	0.4306	0.0694	1/4	0.61
Goodness of fit		Rwp = 12.77 S = 1.38					Rwp = 12.59 S = 1.37					see ref. [9]			
stoichiometry		$Ba_{88}Cu_{90}O_{193}$ ($Ba_{0.98}CuO_{2.144}$)					$Ba_{88}Cu_{93.0}O_{193.0}$ ($Ba_{0.95}CuO_{2.075}$)					$Ba_{88}Cu_{101.4}O_{205.4}$ ($Ba_{0.87}CuO_{2.026}$)			

above strategy, for a pattern collected at $T = 571\,°C$ and $P(O_2) = 9.8 \cdot 10^{-3}$ atm. These results deserve some comments.

- There is a reasonable overall agreement with the single crystal determination as to the atomic coordinates of metal sites. As expected, the agreement is better for the "ordered" part, worse for the "disordered" part.
- For what concerns the occupancy factors of the copper sites, steps b) and c) give Cu4/Cu5 occupancy ratios ($0.304:0.196 = 1.55$, and $0.417:0.335 = 1.24$, respectively) which are on either side of, and not very far from, that given by Paulus et al. [9] (1.38).
- The overall copper content given by step c) corresponds to a $88:93 \cong 0.98:1.03 \cong 0.95$ (Ba:Cu) molecularity. This value is between that obtained by Paulus et al. [9] (i.e. $0.92:1.06 \cong 0.87$), and the stoichiometry of our preparation ($88:90 \cong 0.98$).
- The agreement is clearly worse for the oxygen sites: the O6/O7 ratio ranges from $0.534:0.504 \cong 1.06$ (step b) to $0.564:0.489 \cong 1.15$ (step c), whereas Paulus et al. [9] found 1.38.
- More generally, we found it impossible to determine from profile fitting many parameters concerning the oxygen atoms, because the optimization procedure was divergent for all starting conditions. In particular, we found it necessary to fix the O7 coordinates at the values given by the single crystal determination [9]. For the same reason, we did not try to remove the constraint about total oxygen content from step b) to step c).

Taking into account the complexity of the crystal structure, the different temperature and oxygen pressure conditions, and the obviously better performance of single crystal methods, the agreement might be considered satisfactory.

In conclusion, we may infer that our sample certainly belongs to the crystal structure described in the previous literature. Its molecularity appears as 3% lower than the starting composition of the reagent mixture. While the preparation procedure may be given more credit than the profile fitting, it can also be noticed that the difference between these data is about three times smaller than the discrepancy with previous single crystal determinations. Therefore we can provisionally argue that "$BaCuO_2$" shows a measurable molecularity range, and that the 0.98 (Ba:Cu) ratio is inside its stability field (or very close to its boundary).

Arguments in favor of the stability of the phase when Ba:Cu is near 0.98 are also given by recent EMF measurements [15].

3.2. *Oxygen Stoichiometry*

A reliable determination of oxygen non-stoichiometry is difficult for the reasons already explained in the Experimental Section. Therefore, we systematically supplemented the gravimetric determinations with XRPD patterns recorded *in situ* under a large number of T, $P(O_2)$ conditions, and in the same ranges. Each pattern was inspected for foreign phases, and the lattice constants were determined. Gravimetry measures the mass of the whole *sample*, while XRPD provides information on each *phase* therein. A smooth behavior of *both* measurements as a function of T and $P(O_2)$ gives a more reliable assessment of the single-phase nature of our sample under the investigated ranges of external conditions. Moreover, we always took care of measuring the sample mass at each T, $P(O_2)$ state by approaching the state from both lower and higher temperatures, and to use the various oxygen pressures in a different order for successive samples. Finally, we note that the gravimetric runs provide independent determinations of a) the non-stoichiometry difference from a fixed reference state, and b) the non-stoichiometry of the reference state. Therefore, the *trend* with T and $P(O_2)$ of oxygen stoichiometry is intrinsically more accurate than its absolute value.

The oxygen stoichiometry of $Ba_{0.98}CuO_{1.98+\delta}$ samples is reported in Fig. 3 in the usual form of δ vs. log $[P(O_2)]$ plots. In the whole range of T and $P(O_2)$, the phase has been found to be overstoichiometric, oxygen stoichiometry being approached only at high temperatures under the lowest investigated oxygen activity. The regular trend of oxygen content with temperature is also shown by Figure 4. Both figures show that non-stoichiometry asymptotically approaches an upper value around 0.20–0.21, which may be seen as a property of the crystal structure. It may be interesting to note that this upper limit corresponds to 18 oxygen atoms per unit cell, and the O6 and O7 unoccupied sites account for more than that (not to speak of other possible positions).

Figure 5 shows a similar plot of the lattice constants as a function of temperature and oxygen pressure. The regular trend of both measurements, and in particular the absence of a plateau in the XRPD data and/or a jump in the gravimetric data, is a clear indication that no heterogeneous equilibria occur within the $[T, P(O_2)]$ ranges of the gravimetric determinations. There is some disagreement, here, with previous data. For instance, Migeon et al. [4, 11] reported instability of "$BaCuO_2$" with respect to BaO_2 plus other unknown

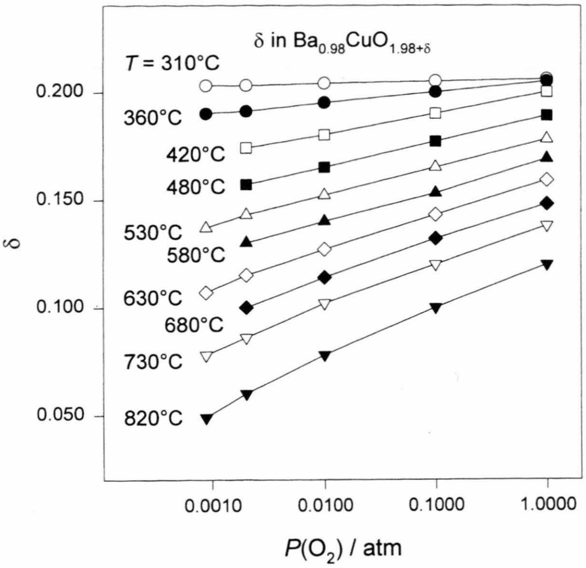

Fig. 3. Oxygen overstoichiometry (δ) of $Ba_{0.98}CuO_{1.98+\delta}$ as a function of oxygen partial pressure (on a logarithmic scale) at different temperatures.

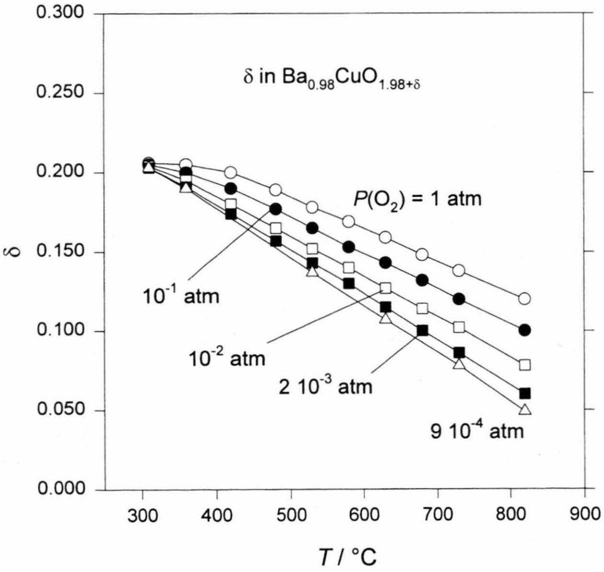

Fig. 4. Oxygen overstoichiometry (δ) of $Ba_{0.98}CuO_{1.98+\delta}$ as a function of temperature at different oxygen partial pressures.

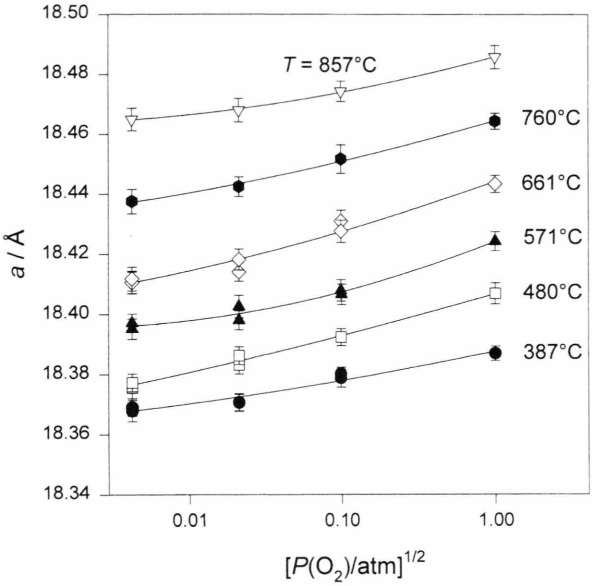

Fig. 5. Lattice constant (*a*) of $Ba_{0.98}CuO_x$ as a function of oxygen partial pressure.

phases, at $P(O_2) > 0.2$ atm. A better agreement can be seen with the results of a recent paper by Maiorova et al. [15], who used TG dynamic measurements at a scan rate of 1 °C/min under a static oxygen atmosphere on a "$BaCuO_2$" sample with Ba:Cu = 1.14.

Generally, we found well reliable gravimetric results starting from the 88:90 cation ratio. Instead, a number of runs with 1:1 cation ratio gave much less reproducible data, with remarkable differences of apparent oxygen stoichiometry between samples and between successive measurements of the same sample. We take this failure as an indication that "$BaCuO_2$" materials with 1:1 cation ratio are indeed polyphasic, at least under most of the *T*, $P(O_2)$ conditions here investigated. Conversely, the reproducible behavior of the 88:90 composition is a further argument in favor of its monophasic nature, which adds to the conclusions of the previous section. Along the same line of arguments, the different Ba:Cu ratio is a reasonable explanation of the disagreement with previous non-stoichiometry data from Migeon et al. [4, 11].

4. Discussion and Conclusions

The usual thermodynamic approach ([27], [28]) to the defect chemistry of simple oxides is based on the assumption of a reference structure, with a well stated oxygen content, and a number of quasichemical equilibria, such as formation of neutral or ionized vacancies or interstitials, coupled with appropriate charge balance constraints. In the algebraic treatment of these equilibria, two approximations are usually made: i) the concentrations (the site fractions) of point defects are identified with the thermodynamic activities (which is an assumption of ideal behavior of the defects), and ii) fixed values are assigned to the concentrations of the regular sites (these values are then typically inserted into the thermodynamic constants and do not appear in the equations of the corresponding equilibria). Both approximations require "low concentrations" of all defects. This assumption hardly holds here. We try here to show that a provisional description of the oxygen non-stoichiometry of "$BaCuO_2$" can indeed be reached by keeping most of the usual machinery, and simply relaxing the approximation of unit concentration of the regular sites. Our approach is based on the assumption that the reference formula is $Ba_{0.98}CuO_{1.98}$, and that the pertinent structure is able to provide a large number of (possibly different) sites for additional oxygen atoms (oxygen interstitials).

Let us start by taking into account only neutral interstitial sites. In the usual approach, the quasichemical equation is

$$\tfrac{1}{2}\,O_2 \rightleftarrows O_i^x \tag{1}$$

with the equilibrium constant

$$K_i = \frac{[O_i^x]}{w}; \quad w \equiv \sqrt{P(O_2)}, \tag{2}$$

and the oxygen over-stoichiometry is given by

$$\delta \equiv [O_i^x] = K_i \cdot w. \tag{3}$$

This equation does not correctly describe the experimental behavior (see Fig. 6), where a saturation effect is clearly apparent.

Now, if the crystal structure provides *s* equivalent interstitial sites per unit formula, (1) implicitly assumes that all these *s* sites are available for each new oxygen entering the structure, whereas only $s - [O_i^x]$ sites are actually available. When $[O_i^x]$ approaches *s*, (3) does not hold, and a saturation effect arises. This effect can be formally described by explicitly writing

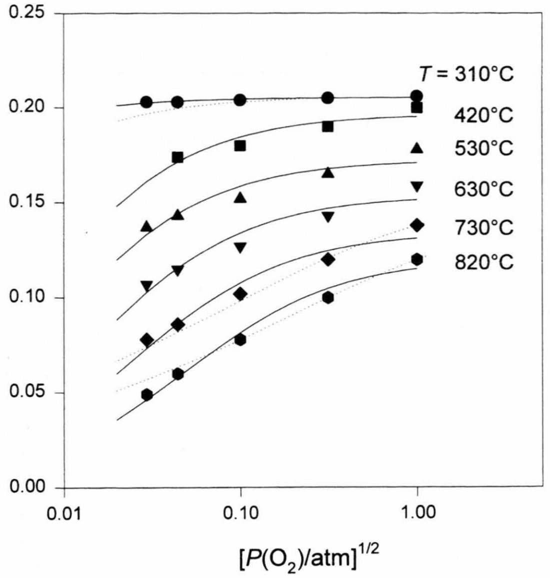

Fig. 6. Fit of the oxygen overstoichiometry (δ) of $Ba_{0.98}CuO_{1.98+\delta}$ with different simplified defect equilibria. Full lines: fit with (6); dotted lines: fit with (10).

the empty interstitial sites V_i^x in the quasichemical equilibrium:

$$\tfrac{1}{2}\,O_2 + V_i^x \rightleftarrows O_i^x, \quad K_i = \frac{[O_i^x]}{w \cdot [V_i^x]} \tag{4}$$

with the site balance

$$[O_i^x] + [V_i^x] = s. \tag{5}$$

Equations (4) and (5) give a Langmuir-type equation

$$\delta = [O_i^x] = K_i\, s\, \frac{w}{1 + K_i w}, \tag{6}$$

which describes a (qualitatively) correct behavior ($\delta \to s$ when $w \to \infty$): the continuous line of Fig. 6 shows the fit of experimental data with (6).

I should be noted that oxygen stoichiometry saturates at $\delta = s$ also if one adds to (4) and (5) one or more defect ionization equilibria, although the functional dependence of δ on oxygen activity is no longer given by (6). The point can be illustrated by considering, for example, the ionization equilibrium

$$O_i^x \rightleftarrows O_i'' + 2\,h^\bullet; \quad K_2 = \frac{[O_i'']\,p^2}{[O_i^x]}; \quad p \equiv [h^\bullet] \tag{7}$$

with the charge balance

$$2\,[O_i''] = p, \tag{8}$$

Then, using for simplicity the further assumption

$$[O_i''] \gg [O_i^x], \tag{9}$$

(4), (7), and (8) give

$$w = \frac{\delta^3}{4\,K_i\,K_2\,(s-\delta)}. \tag{10}$$

The experimental data are in qualitative agreement also with (10), as shown by the dotted lines in Figure 6.

It should be clear that the saturation behavior ($\delta \to s$ when $w \to \infty$) shown by the experimental data cannot be explained by the ionization equilibrium (7) and (8) alone. This can be clarified by considering, as an example, the case of equilibrium (1) with both neutral and completely ionized interstitials, (7), (8). Then, the δ vs. w trend is given by

$$\delta = [O_i^x] + [O_i''] = K_i \cdot w + \sqrt[3]{K_i\,K_2/4} \cdot w^{1/3},$$

which cannot be accepted because it does not describe a saturation behavior. This conclusion holds very generally, and can be rigorously proved using, for instance, a method discussed previously [29]. It can briefly be said here that the statement relies on the monotonic (increasing) trend of p as a function of w, in particular that p goes as $w^{1/n}$, where n is slowly varying with w, within $2 \leq n \leq 3$.

Because of the exceedingly complicated crystal structure of the present phase, we do not deem it possible, however, to derive from the non-stoichiometry determinations a more precise description of the defect equilibria, and to offer quantitative values of the equilibrium constants. In particular, it is not unreasonable to argue that a number of (non-equivalent) interstitial sites are actually available, and that the relative energy positions of these sites can be temperature-dependent, because of thermal expansion. Finally, the problem of ionization equilibria will be better described in the following part II on the basis of electrical conductivity and thermopower measurements.

In conclusion, we have investigated "$BaCuO_2$" materials under a wide range of temperature and oxygen partial pressure conditions. The bad reproducibility of the 1:1 (Ba:Cu) composition indicates that this material is very probably polyphasic. Instead, the 88:90 composition is proved monophasic by the regular trend of coupled gravimetric and diffractometric determinations, in agreement with other literature data [15]. The latter material is oxygen over-stoichiometric over the whole investigated T (300 ÷ 820 °C) and $P(O_2)(1 \div 3 \cdot 10^{-3}$ atm) ranges. At low temperatures, the over-stoichiometry approaches $\delta = 0.21$ [in $Ba_{0.98}CuO_{1.98+\delta}$].

The behavior of non-stoichiometry is consistent with the presence of oxygen interstitials with a limiting value of available interstitial sites. However, it is not possible to specificy whether neutral or charged interstitials are involved. On the basis of the δ vs. $P(O_2)$ curves and of the crystal structure it is suggested that different interstitial sites are involved.

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