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STUDIES ON THE OXYGEN STOICHIOMETRY IN SUPERCONDUCTING CUPRATES BY THERMOANALYTICAL METHODS

M. Karppinen, L. Niinistö[1] and H. Yamauchi*

Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226, Japan
[1]Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology,
FIN-02150 Espoo, Finland

Abstract

Thermoanalytical methods provide important means for studying oxygen stoichiometries in high T_c superconducting cuprates. The optimum annealing temperature for a desired oxygen content in the superconducting product or in related materials can be established by thermogravimetric measurements. By performing the final annealing in a thermobalance the amount of the incorporated or released oxygen can be conveniently both controlled and determined. Furthermore, the absolute oxygen content in the end product can be analyzed by the thermogravimetric reduction method. Finally, the stability of the oxygen content under various atmospheres can be checked utilizing either thermogravimetric or differential thermal analysis techniques. The potential and applications of thermal analysis within the above themes of cuprate superconductor research are reviewed and discussed using illustrative examples from the authors' own experimental works as well as from the literature.

Keywords: oxygen stoichiometry, superconductors, themal analysis

1. Introduction

The superconducting properties of all oxide superconductors are closely related to mixed valence states of metals, controlled by chemical substitutions and the oxygen stoichiometry of the material [1]. In the case of the high T_c (critical temperature of superconductivity) superconducting cuprates the transition temperature depends crucially on the carrier concentration, generally referred to as the amount of excess charge in the CuO_2 layers or the valence of copper. Increasing the oxygen content will, in principle, increase the copper valence value and *vice versa*. Without reliable knowledge of the oxygen stoichiometries the properties of the studied samples can not be interpreted.

The potential provided by thermoanalytical methods to study oxygen stoichiometries in the cuprate superconductors was realized very soon after the dis-

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* Permanent address: Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology, FIN-02150 Espoo, Finland.

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covery of these fascinating compounds [2–4]. In the present review this topic is discussed with selected examples from the authors' own experiments as well as from the literature data with special emphasis on the applications of thermogravimetry.

2. Studies on the annealing effects

A common feature of perovskite oxides is the ability to absorb and desorb oxygen reversibly within certain limits set by the structure [5]. High T_c cuprate superconductors possess perovskite related structures, and show variable oxygen contents as well. Most prominent changes in oxygen stoichiometry are detected in the $REBa_2Cu_3O_{7-y}$ and $Pb_2(Sr,Ba)_2(RE,Ca)Cu_3O_{8+y}$ (*RE*= rare earth element) phases. Because of the sensitivity of the oxidation degree for the synthesis conditions, successful formation of the desired superconducting structure does not automatically ensure that the properties of it are optimized from the superconductivity point of view but postannealing treatments in oxygen partial pressures, higher or lower than used for the synthesis, are often needed. Also, in order to prepare series of samples with varying oxygen contents, postannealings under tightly controlled conditions are essential to attain the desired stoichiometries. Temperature, oxygen partial pressure and the cooling rate are the important parameters during the last annealing. Thermogravimetry can be used for establishing the appropriate annealing conditions, for the *in situ* detection of the amount of incorporated or released oxygen during the annealing performed in a thermobalance as well as for following the changes in the oxygen stoichiometry during various thermal cycles. In Sections 2.1–2.3 examples of such studies are discussed.

2.1. Investigation of the oxygen stoichiometry during various thermal cycles

The early results of the thermogravimetric experiments on the oxygen stoichiometry of $YBa_2Cu_3O_{7-y}$ during various thermal cycles were essential to learn the importance of the slow cooling under an atmosphere of sufficient oxygen partial pressure for the superconductivity of this compound [6–11]. During the high temperature synthesis of $YBa_2Cu_3O_{7-y}$ the oxygen deficient, tetragonal phase is first formed. When cooling slowly down in an oxygen-rich atmosphere the tetragonal phase turns into the superconducting orthorhombic form by accommodating oxygen into the structure. The kinetics of the oxygenation/deoxygenation processes have been studied by Tang and Lo [12] by means of TG (thermogravimetry) measurements, and found to be diffusion-controlled with an activation energy of 1.3 eV for samples having y close to 0.1. The chemical diffusion coefficient for a powder sample was determined to be 10^{-10} cm^2 s^{-1} at 500°C. This number is two to three orders of magnitude smaller than values reported for sintered samples [13, 14]. In the case of large or highly dense samples (e.g. single crystals) very slow cooling rates or an additional annealing in flowing oxygen at temperatures between 400 and 500°C are required for the complete oxidation. The highest oxygen content achieved for $YBa_2Cu_3O_{7-y}$ powders by long annealings in flowing oxygen around 400°C is slightly below (y=0.04 [15]) the stoichiometric value.

The oxygen release and uptake processes are reversible if the heating and cooling cycles are carried out under same atmosphere, as can be seen from the TG curves in Figs 1a–c [15]. The mass loss of a fully oxidized material starts at about 350°C in both oxygen and nitrogen atmospheres (Figs 1a and b). Subsequent heating results in the oxygen-deficient phase of $y=1.0$ around 750°C in N_2 and above 900°C in O_2, the exact temperatures depending on the heating programme. Upon cooling down to room temperature the initial oxygen stoichiometry is recovered only in the case of oxygen atmosphere (Fig. 1a). On the other hand, by recycling in O_2 the oxygen content of an oxygen-deficient sample can be increased again (Fig. 1c). Upon heating the oxygen incorporation starts already below 200°C. The maximum mass is reached at 360°C, at which temperature the oxygen incorporation and release processes are balanced. According to DTA (differential thermal analysis) measurements by Shelby *et al.* [16] the oxygen release process is endothermic, while the subsequent incorporation of oxygen corresponds to an exothermic peak.

Kishio *et al.* [17] have determined by combined iodometric and thermogravimetric analyses the equilibrium values of oxygen stoichiometry in the $YBa_2Cu_3O_{7-y}$ system at different temperatures (350–1000°C) as a function of oxygen partial pressure in a range of 10^{-4}–1 atm (Fig. 2). No discontinuity in y is observed against the oxygen pressure around the tetragonal/orthorhombic phase transition area, indicating that the transition is higher than of first order. In a TG curve the phase boundary is seen as a distinct inflection in the TG curve or as a minimum or maximum in the DTG (differential thermogravimetry) curve. The structural phase transition is not located at any constant oxygen content value but depends on the pressure [18]. According to Kubo *et al.* [19] the phase boundary has a slope of $dy/dT = -4.7\times10^{-4}\ K^{-1}$. In the $REBa_2Cu_3O_{7-y}$ system the transformation temperature tends to increase with decreasing ionic radii of the rare earth element [20]. Furthermore, the oxygen deficiency at the transformation point increases with increasing transformation temperature. Replacing yttrium partly by calcium, on the other hand, does not increase the average copper valence but the trivalent to divalent substitution is counteracted by a decrease in oxygen content when the material is synthesized under ambient pressure. Otherwise the obtained TG curves for the $(Y,Ca)Ba_2Cu_3O_{7-y}$ system under various atmospheres are very similar to those of corresponding non-doped samples [21].

In the $HgBa_2CaCu_2O_{6+y}$ compound as well, the oxygen release starts above 350 °C in an inert atmosphere. Confirmed by mass spectrometric analysis of Xu *et al.* [22], the mass loss seen in TG curves (Fig. 3) below that temperature is due to evaporation of mercury, probably existing in metallic form in grain boundaries. Evolution of oxygen was detected by mass spectrometry between 350 and 450°C. At the same temperature range a small but broad endotherm can be observed superimposed on the baseline of a QDTA (quantitative differential thermal analysis) curve (Fig. 3). The mass losses above 600°C are already associated with the decomposition of the material. On the other hand, if oxygen-deficient $HgBa_2Ca_{n-1}Cu_nO_{4+2}$ samples are post-annealed the temperature corresponding to the maximum oxygen incorporation depends both on n and the oxygen partial pressure. According to

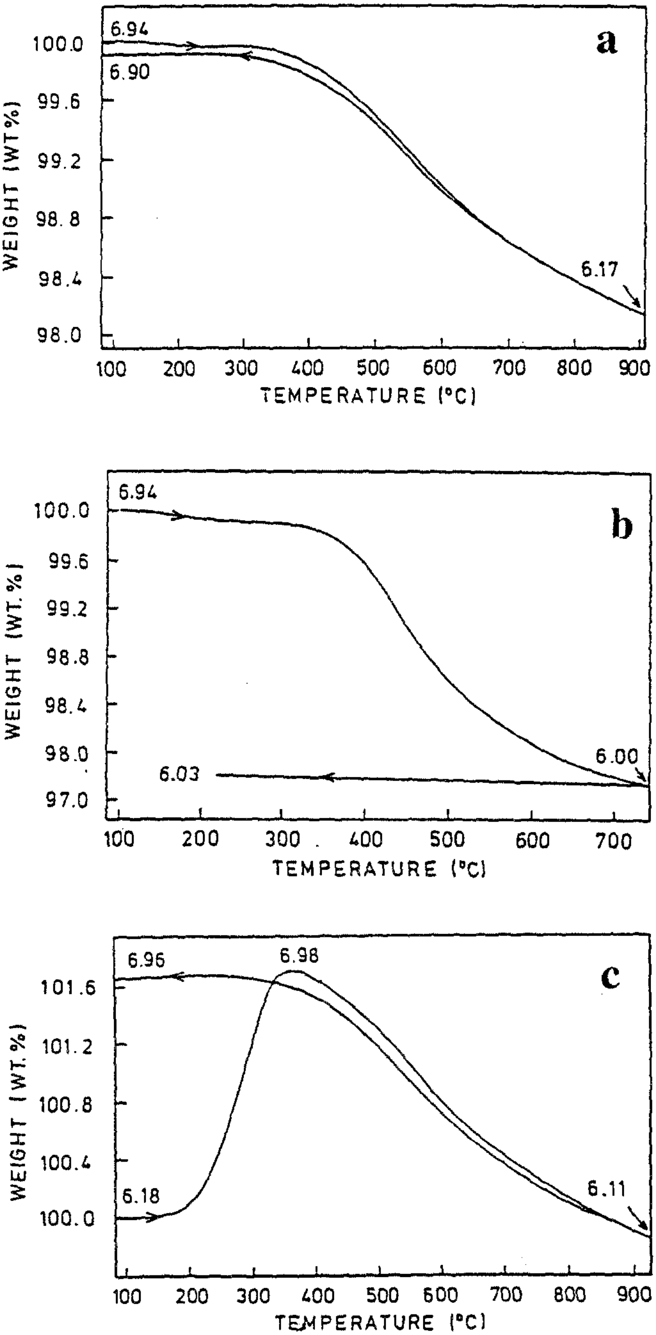

Fig. 1 Heating and cooling TG curves for a) $YBa_2Cu_3O_{6.94}$ in O_2, b) $YBa_2Cu_3O_{6.94}$ in N_2 and c) $YBa_2Cu_3O_{6.16}$ in O_2 (after [15])

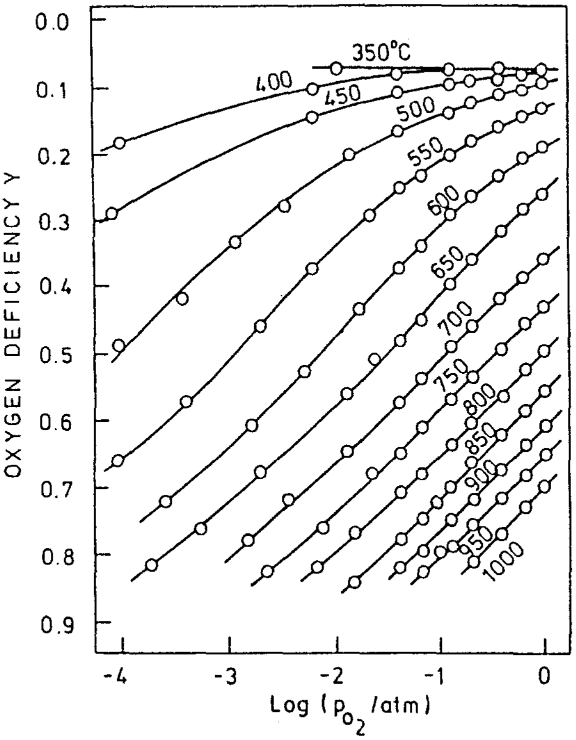

Fig. 2 Oxygen deficiency y in $YBa_2Cu_3O_{7-y}$ at different temperatures as a function of O_2 partial pressure (after [17])

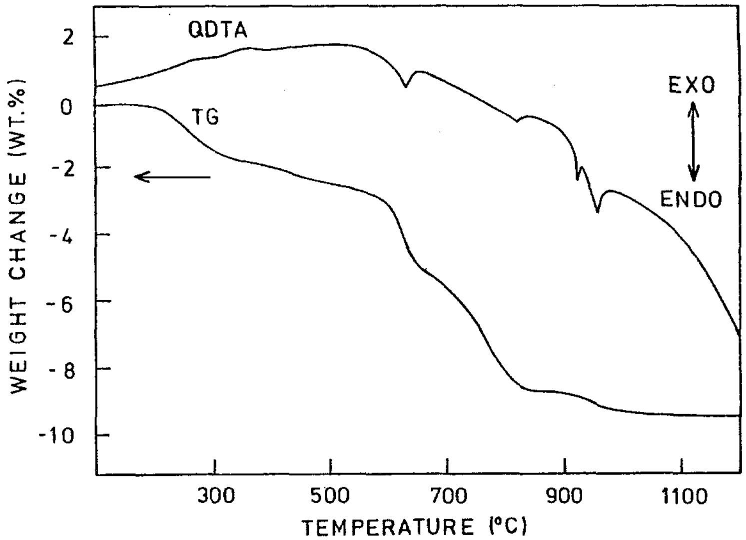

Fig. 3 Simultaneous TG/QDTA curves for the heating of $HgBa_2CaCu_2O_{6+y}$ in Ar (after [22])

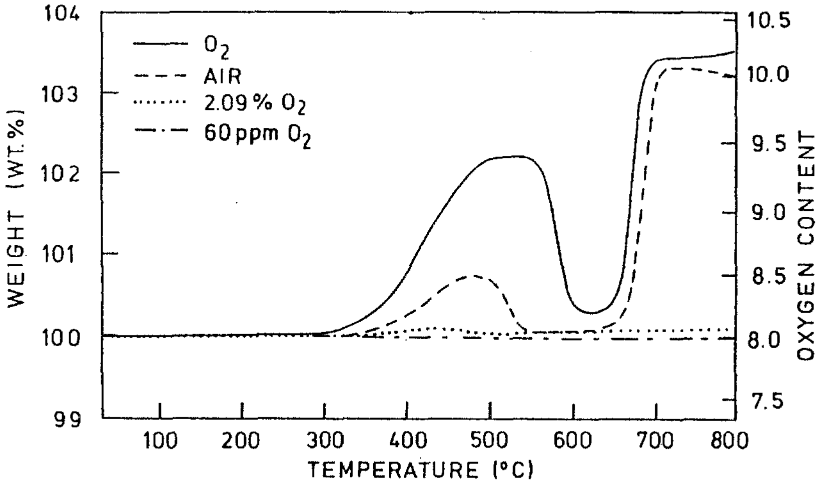

Fig. 4 Heating TG curves for $Pb_2Sr_2YCu_3O_{8+y}$ (y close to 0, but not determined) in various atmospheres (after [26])

Tokiwa-Yamamoto *et al.* [23] this temperature increases from 204 to 268°C in an oxygen atmosphere (1 atm) when going from the $n=1$ phase to the $n=3$ phase. A decrease in the oxygen partial pressure by a factor of 10 seems to increase the optimum O_2-loading temperature by *ca.* 10°C. With decreasing O_2 partial pressure also the amount of incorporated oxygen is decreased.

In the case of the Tl-based superconductors decomposition due to the loss of thallium is observed around 600°C. According to TG measurements the mass change of the $Tl_2Ba_2CuO_z$ phase, corresponding to *ca.* 0.2 oxygen atoms per formula unit, is reversible up to 585°C [24, 25].

The oxidation-reduction behaviour in the $Pb_2(Sr,Ba)_2(RE,Ca)Cu_3O_{8+y}$ system is more complex than in other superconducting cuprates. This is partly due to the thermodynamic stability of simple Pb(IV) perovskites under oxidizing conditions. Therefore, mildly reducing atmospheres are needed for the synthesis of the superconducting phase. Gallagher *et al.* [26] have by means of TG and DTA measurements systematically studied the effects of oxygen partial pressure and temperature on the oxygen content in various oxygen deficient $Pb_2Sr_2(RE,Ca)Cu_3O_{8+y}$ samples. Under O_2-containing atmospheres the oxygen deficient material is reversibly oxidized at 300–600°C. The extent of the oxidation-depends on the heating rate and oxygen partial pressure (Fig. 4), but a very wide range of oxygen stoichiometries is tolerated by the structure. Around 500°C the oxygen content exhibits a maximum. The oxidative decomposition occurring above 630°C is irreversible.

2.2. *Search for appropriate conditions for the final annealing*

Quenching from the high synthesis temperatures leads to oxygen-deficient materials having inhomogeneous oxygen distribution. In order to prepare oxygen-deficient $YBa_2Cu_3O_{7-y}$ samples without an oxygen gradient various gettering techniques

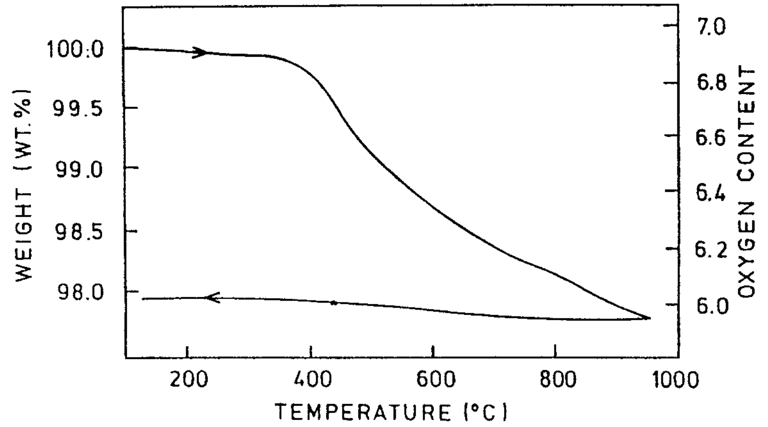

Fig. 5 Heating TG curve for $YBa_2Cu_3O_{6.9}$ in N_2 (after [28]). From this curve the proper temperature (corresponding to the desired oxygen content) for the postannealing in N_2 can be read when oxygen-deficient $YBa_2Cu_3O_{7-y}$ samples ($0.1 < y < 1.0$) are prepared

have been successfully applied [27], but postannealing of oxygen-saturated material in a flowing inert atmosphere at a fixed equilibrium temperature has proven to be another useful possibility [28]. The proper temperature corresponding to the desired oxygen content can be read from a TG curve measured for the oxygen saturated starting material (Fig. 5). The reliability of the obtained oxygen content values can still be checked e.g. by iodometric titrations [28] or by utilizing the thermogravimetric reduction technique (Section 3.1).

2.3. In situ detection of the amount of incorporated or released oxygen during annealing

The amount of incorporated or released oxygen is most conveniently controlled and determined by performing the annealing in a thermobalance. In [29, 30] this kind of controlled-oxygen-loading results for a $Pb_2Ba_2EuCu_3O_{8+y}$ sample have been reported. Before the oxygen annealing the oxygen excess y of the as-synthesized material was established ($y=0.16\pm0.02$) by a coulometric titration technique [31, 32]. As can be seen from the obtained TG and DTG curves (Fig. 6), the mass gain starts above 250°C. The optimum temperature for the oxygen-loading seems to be around 350°C, at which temperature the incorporation is fastest. The TG data of three parallel oxygen annealings revealed mass gains corresponding to 1.63±0.01 oxygen atoms per formula unit. This means that the oxygen content ($8+y$) of the sample after the oxygen-loading is 9.79±0.03. In [33] the same method has been used to prepare a series of $Pb_2Sr_2Eu_{0.75}Ca_{0.25}Cu_3O_{8+y}$ samples with varying oxygen content. Capponi *et al.* [34], on the other hand, have monitored thermogravimetrically the amount of incorporated oxygen into an oxygen-deficient $Pb_2Sr_2YCu_3O_{8+y}$ sample at a constant temperature of 447°C as a function of time (Fig. 7). The mass gain was stabilized in ten hours, corresponding to an oxygen content increase by about 1.90

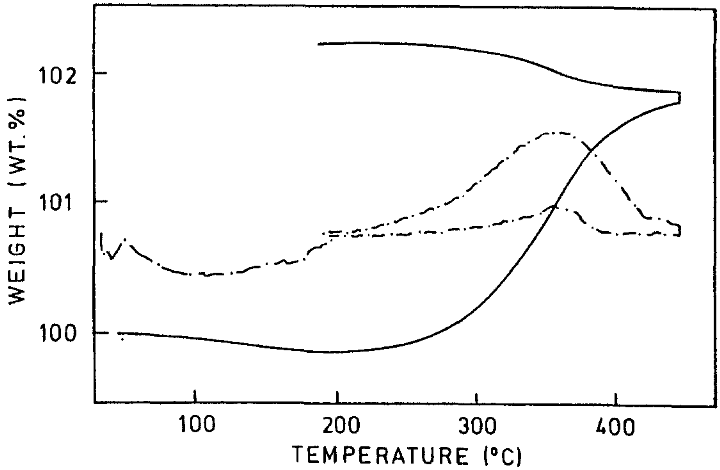

Fig. 6 TG (solid line) and DTG (broken line) curves for the *in situ* oxidation of $Pb_2Ba_2EuCu_3O_{8.16}$ in O_2 (after [29])

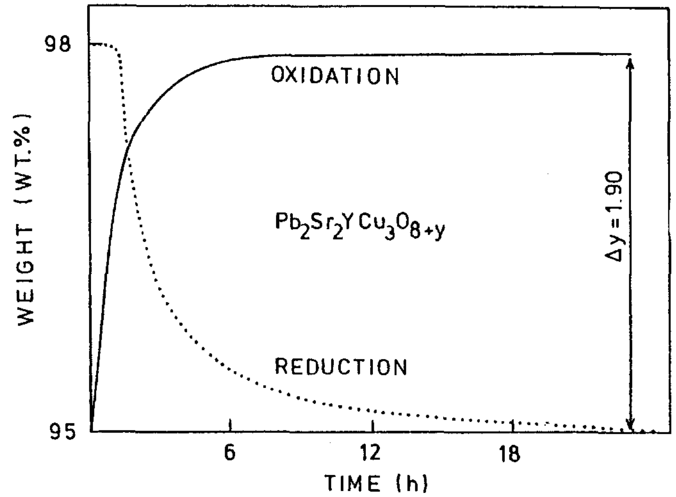

Fig. 7 Isothermic TG curves for the *in situ* oxidation at 447°C in O_2 (solid line) and reduction at 497°C in N_2 (broken line) of $Pb_2Sr_2YCu_3O_{8+y}$ (after [34])

atoms per formula unit. Conversely, when the final product was heat treated at 497°C in nitrogen it lost the same amount of oxygen.

Oxygen-deficient $YBa_2(Cu,Fe)_3O_{7-y}$ samples have been synthesized by Kallias *et al.* [35] by removing oxygen from the as-prepared material in a thermobalance under flowing argon. The samples were heated at a rate of 4°C min^{-1}, and when the desired value of y was achieved, the sample was cooled down to RT as fast as possible.

Finally for comparison, oxygen-depletion results for the simple $LaCuO_3$ perovskite are shown in Fig. 8 [36]. Based on its chemical and structural properties,

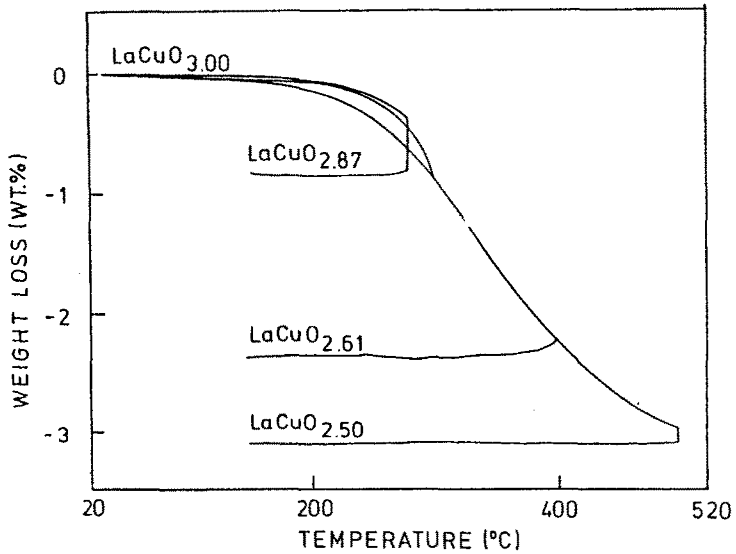

Fig. 8 TG curves for the *in situ* oxygen depletion of $LaCuO_3$ in Ar (after [36])

highly related to those of the cuprate superconductors, the $LaCuO_{3-y}$ system has been considered as a potential candidate for exhibiting superconductivity when optimally doped. The $LaCuO_{3-y}$ framework is stable over a remarkably wide oxygen stoichiometry range, *i.e.* $0 \leq y \leq 0.5$, enabling the tuning of the copper valence value continuously from +3.0 to +2.0. In this case, however, the oxygen release is not reversible under an ambient atmosphere since the highly oxidized stoichiometric $LaCuO_3$ form is stabilized only under very high oxygen pressures.

3. Determination of the absolute oxygen content

Since the oxygen content of the end product is one of the crucial characteristics of the high T_c cuprates determining the carrier concentration and further the critical temperature, several methods of chemical analysis have been applied to establish the absolute values of this parameter in different superconducting phases and related materials [37]. Besides the most widely used wet chemical redox methods, various thermogravimetric approaches have been adapted as well for the studies of superconducting cuprates. The absolute oxygen content can be determined by measuring the mass loss accompanying either the synthesis or the total reduction of the sample. Using a standard reference sample with an identical metal composition and a known oxygen content, the unknown oxygen content can also be calculated from the difference in the mass loss under an inert atmosphere detected by TG for the studied sample relative to the standard one. From these three different thermoanalytical possibilities, the reduction method is preferred since the measurement connected to the synthesis of the material can not be repeated for already existing samples and the inert atmosphere TG method always requires a good reference sample.

3.1. Thermogravimetric reduction

In the thermogravimetric reduction method the sample is heated to high temperatures in a reducing atmosphere. The amount of oxygen in the starting material can be calculated from the total mass loss during the thermal treatment if the reduction products are known. This method has been applied for the studies of high valent copper compounds already before the time of superconducting cuprates, e.g. for $KCuO_2$ in 1973 [38] and $(La,Sr)_2CuO_{4-y}$ in 1981 [39]. For the oxygen content studies of high T_c cuprates the TG reduction method has also been used from the very beginning [40–46].

Hydrogen is the most commonly used reductant, but if the reduction is performed with CO the carbon dioxide gas formed can be additionally detected by IR spectroscopy [47]. Superconducting cuprates may dissolve hydrogen to some extent (e.g. $YBa_2Cu_3O_7H_{0.6}$ at 1 atm H_2 [48]) at low temperatures. The hydrogen-containing compounds formed are, however, metastable and decompose to the stable reaction products of metallic copper and various alkaline earth and rare earth oxides at higher temperatures [49]. The initial weight gain corresponding to the hydrogen incorporation is often difficult to detect within the accuracy of the measurement. In Fig. 9 a typical reduction TG curve for the $YBa_2Cu_3O_{7-y}$ compound is shown. Heating the sample under a H_2/Ar atmosphere results in a selective reduction of copper to metallic state by 950°C, the exact temperature depending strongly on the hydrogen partial pressure in the reductant gas [50]. Yttrium and barium are maintained in the reduction process as oxides. The stabilities of Y_2O_3 and BaO under the conditions concerned have been confirmed by Vlaeminck *et al.* [51] up to 1000°C.

The overall mass loss corresponding to the reduction reaction of $YBa_2Cu_3O_{7-y}$ (Eq.(1)) may vary from 6.15% ($y=1$) to 8.41% ($y=0$). It is essential to follow the reaction with a thermobalance of high sensitivity and to determine the mass loss at 950°C, because during cooling the mass of the sample gradually increases due to the reaction of BaO with moisture or CO_2, forming $Ba(OH)_2$ or $BaCO_3$, respec-

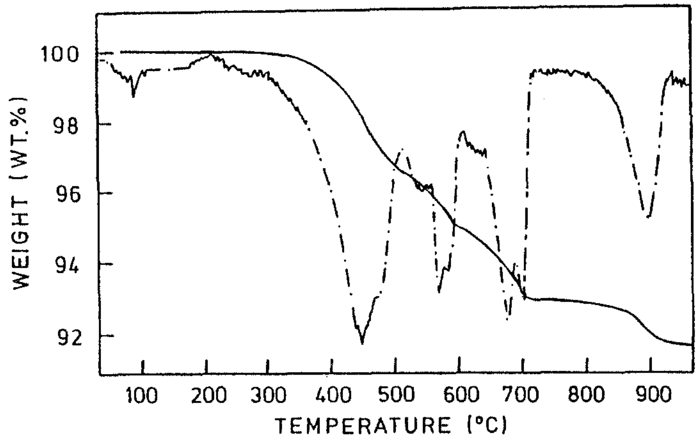

Fig. 9 Hydrogen reduction TG (solid line) and DTG (broken line) curves for $YBa_2Cu_3O_{7-y}$ (after [4])

tively. In order to get highly accurate results the effects of buoyancy, resulting in mass gain equal to the mass of gas displaced by the sample, and other aerodynamic forces have to be taken into account. The total experimental correction, necessary to compensate these effects, corresponds to an error of *ca.* 0.01–0.02 in the oxygen deficiency value y [51].

$$\begin{gathered}2YBa_2Cu_3O_{7-y}+(7-2y)H_2 \rightarrow \\ Y_2O_3+4BaO+6Cu+(7-2y)H_2O \qquad (1)\end{gathered}$$

The loss of mass is stepwise when an $YBa_2Cu_3O_{7-y}$ sample is reduced. Gallagher *et al.* [52] have studied the intermediate products by interrupting the reduction process at several temperatures; X-ray diffraction (XRD) measurements did not, however, reveal any obvious intermediates, probably because of poor crystallinity or due to partial reaction of the Ba and *RE* oxides to hydroxides or hydroxide hydrates with the water vapour. It is, however, believed that the reduction process of $YBa_2Cu_3O_{7-y}$ starts with the removal of oxygen from the Cu–O chains [51, 53, 54]. This can be seen e.g. by comparing the reduction curves obtained for $YBa_2Cu_3O_{7-y}$ samples with y varying between 0 and 1; the mass loss around the temperature range 350–500°C correlates well with the initial oxygen content, while the changes at higher temperatures than 500°C are rather independent of the oxygen content of the starting sample. Consistently, the reduction curve of the Y_2BaCuO_5 phase (no Cu–O chains in the structure) does not exhibit any mass changes below 400°C. A complete TG analysis gave a stoichiometry of $Y_2BaCuO_{5.006}$ for this non-superconducting reference compound [51]. The last plateau around 800°C in the reduction curve of $YBa_2Cu_3O_{7-y}$ corresponds most probably to Cu_2O and 2Cu. The Cu(I) oxide is much more stable than CuO, which is reduced in a single step around 300°C [51, 55].

Besides the above discussed studies on the $YBa_2Cu_3O_{7-y}$ compound, the TG reduction method has been successfully applied to the oxygen content evaluation of other *RE* based cuprates, e.g. La_2CuO_{4-y} [56] and Nd_2CuO_{4-y} [57], as well.

The accuracy of the TG reduction method may be limited by difficulties in defining either the resulting reduction products or the end point of the reduction pro-cess [58]. Even in the case of the reduction of $YBa_2Cu_3O_{7-y}$ formation of small amounts of $Y_2Cu_2O_5$ has been suggested [59]. On the other hand, in the reduction residue of $LaBa_2Cu_3O_{7-y}$ the existence of the following components (in order of their relative content) has been detected by careful XRD analyses: Cu, BaO, $LaCuO_2$, $BaCuO_2$, Ba, La_2O_3, La and CuO [60]. This means that estimations about the oxygen content of the starting $LaBa_2Cu_3O_{7-y}$ material can not be done in such a straightforward way as in the case of the yttrium based compound. Song *et al.* [60] have used a kind of reverse approach to establish the oxygen contents in $LaBa_2Cu_3O_{7-y}$ samples: the final degree of the reduction is supposed to be equal after the H_2/Ar treatment at 900°C in all samples having a similar metal stoichiometry. This degree is defined using a stoichiometric mixture of La_2O_3, $BaCO_3$ and CuO as a reference sample. Once the final oxygen content after the reduction is known, the initial oxygen content in the studied sample can be easily calculated from the observed mass loss. Furthermore, although rare earth elements are found to remain at least mostly as oxides, some of them exhibit two possible oxidation states. In [50 and 61] reduction data on europium containing samples have been reported. No sign of divalent oxide was found either in the high temperature X-ray diffraction simulation of the thermogravimetric reduction or in the Mössbauer study of the reduction residue [61].

Oxygen content analysis by means of thermogravimetric reduction is also complicated by the presence of easily volatilized metals, and thus can not be recommended for the Bi-, Pb, Tl- or Hg-based materials. It has been, however, applied in the cases of bismuth [61–65] and lead [66] cuprates by taking care to avoid loss of these metals during the thermal treatment. The single step reduction reactions to

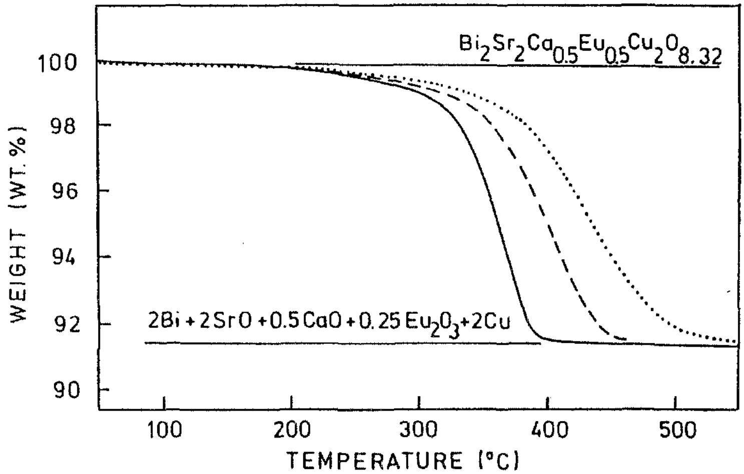

Fig. 10 Hydrogen reduction TG curves for $Bi_2Sr_2Ca_{0.5}Eu_{0.5}Cu_2O_{8+y}$ recorded using heating rates of 2 (solid line), 5 (broken line) and 10°C min^{-1} (after [61])

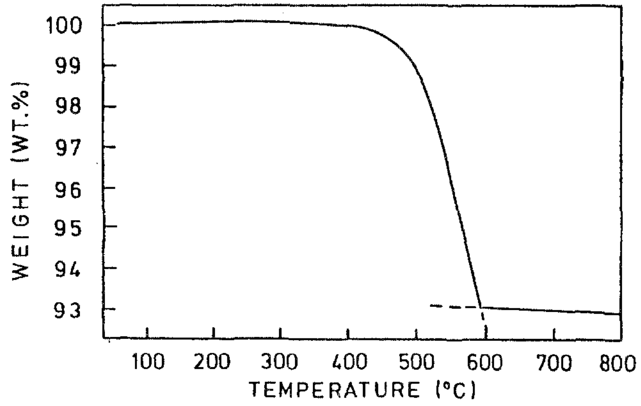

Fig. 11 Hydrogen reduction TG curve for $Pb_2Sr_2YCu_3O_{8+y}$ (after [66]). The additional mass loss seen beyond 600°C is due to the evaporation of lead

metallic copper and bismuth (Eq. (2)) or lead (Eq. (3)) are completed around 500–600°C, the exact temperatures depending on the heating programme [61]. The additional changes in the sample mass seen sometimes in the thermograms (Figs 10 and 11) beyond these temperatures are due to the evaporation of Bi or Pb metals.

$$\begin{gathered} Bi_2Sr_2CaCu_2O_{8+y}+(5+y)H_2 \rightarrow \\ 2Bi+2SrO+CaO+2Cu+(5+y)H_2O \end{gathered} \tag{2}$$

$$\begin{gathered} Pb_2Sr_2YCu_3O_{8+y}+(4.5+y)H_2 \rightarrow \\ 2Pb+2SrO+0.5Y_2O_3+3Cu+(4.5+y)H_2O \end{gathered} \tag{3}$$

In the case of $YBa_2Cu_3O_{7-y}$ the thermogravimetric reduction method sometimes tends to give somewhat higher oxygen content values than the various titration methods [55, 67]. This discrepancy has been explained by the presence of unreacted $BaCO_3$ which decomposes in the thermobalance increasing the observed mass loss considerably even as small amounts [55]. On the other hand, although the possible volatilization of Bi metal might easily cause overestimated oxygen contents for the bismuth cuprates when analyzed by the H_2/TG method, such unusually large values have not been observed [68].

3.2. Thermogravimetric detection of the mass loss under an inert atmosphere

The $(La,Sr)_2CuO_{4+y}$ samples synthesized under ambient conditions are considered to possess rather constant oxygen content values close to $y=0$, but excess oxygen above the stoichiometric value can be introduced into the structure by means of high pressure, electrochemical, "soft chemical" or plasma oxidation techniques. In thermogravimetric oxygen content analyses carried out under an inert atmosphere as-synthesized material can be used as a reference for the oxidized samples. Rial *et al.* [69] have studied oxygen stoichiometries in two $(La_{1-x}Sr_x)_2CuO_{4+y}$ ($x=0.025$ and 0.045) samples oxidized chemically by hypobromite. In an argon atmosphere the as-synthesized samples underwent at 250°C a very small mass loss corresponding to $y=0.01$, while two overlapping mass losses beginning at temperatures around 160 and 260°C were detected for the oxidized samples (Fig. 12). The excess oxygen was totally released by 300°C. The observed total mass losses for the oxidized $x=0.025$ and 0.045 samples correspond to the y values of 0.13 and 0.11, respectively.

3.3. In situ synthesis of superconductors in a thermobalance

Kao and Ng [70] have used a very straightforward TG approach to investigate oxygen contents in various bismuth cuprates. In their method the mass changes occurring during the heat treatment processes simulating the normal synthesis conditions are continuously monitored for different mixtures of Bi_2O_3, $SrCO_3$, CaO and CuO starting powders. Since the stoichiometry of their quaternary mixture ($Bi_2O_3+2SrCO_3+2CaO+4CuO$) does not correspond to any of the compositions of

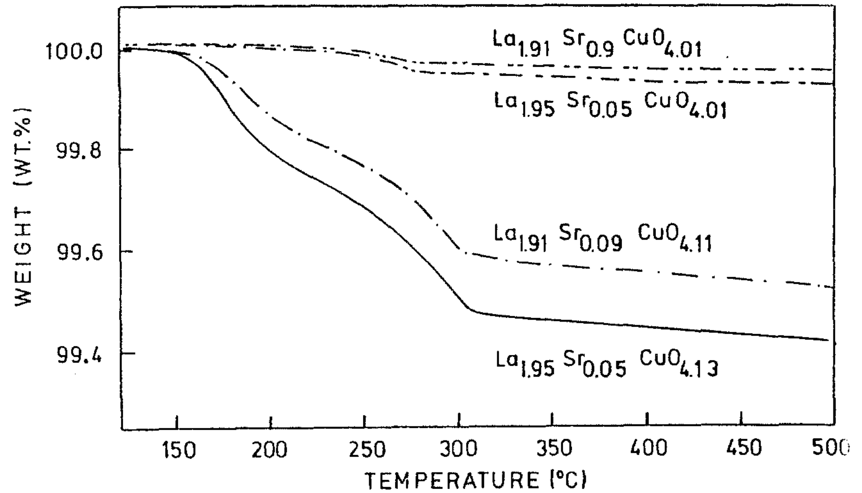

Fig. 12 Heating TG curves for as-synthesized (y=0.01) and "soft chemically" oxidized $(La_{1-x}Sr_x)_2CuO_{4+y}$ (x=0.024 or 0.045) samples in Ar (after [69]). The oxygen contents of the oxidized samples can be calculated using the corresponding as-synthesized samples as reference materials

$Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n+y}$ superconductors, further interpretation of the obtained oxygen excess values (0.38 after the first heat treatment cycle in oxygen) is difficult, however.

4. Examples of other studies

Besides the most widely applied techniques and methods to study the oxygen contents and annealing effects in superconducting cuprates (discussed in Chapters 2 and 3), various other interesting thermoanalytical approaches have been utilized. In Sections 4.1–4.4 some examples of recent studies are given.

4.1. Vapor pressure studies on the oxygen stoichiometry in $YBa_2Cu_3O_{7-y}$

Results of an extensive vapor pressure study on the oxygen stoichiometry in $YBa_2Cu_3O_{7-y}$ as a function of temperature (400–900°C) and oxygen pressure (up to 1 atm) have been reported by Guskov *et al.* [71]. The oxygen contents of the studied samples were analyzed by the iodometric titration method as well. By taking the reported data as a standard, vapor pressure scanning can be used for the precise determination of the absolute oxygen content in $YBa_2Cu_3O_{7-y}$ samples.

4.2. Oxygen isotope studies in $YBa_2Cu_3O_{7-y}$

Isotope effect studies, especially experiments concerning oxygen isotopic substitutions, are considered to be important for the understanding of the mechanism of high T_c superconductivity. As the observed isotope effects are small, it is important to use well characterized samples. $YBa_2Cu_3O_{7-y}$ samples with high ^{18}O content can

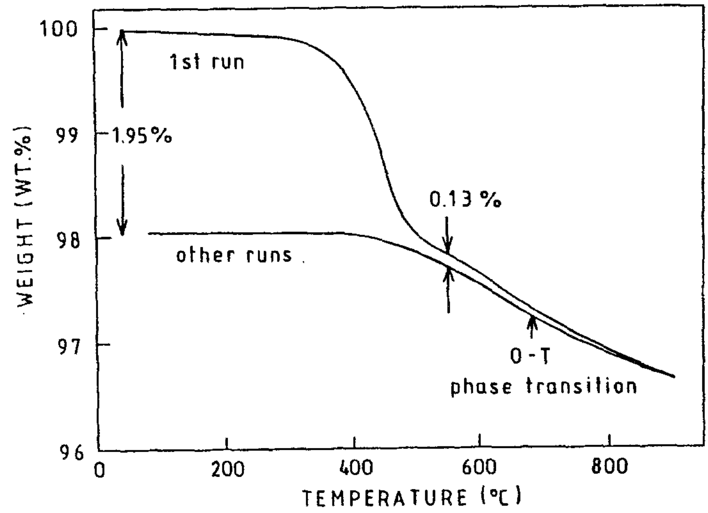

Fig. 13 TG curves for the isotope exchange in an ^{18}O-enriched $YBa_2Cu_3O_{7-y}$ sample (after [72])

be prepared by oxidizing Y, Ba and Cu metals in $^{18}O_2$ atmosphere. The resulting isotope content can be easily determined with a simple thermogravimetric experiment, since in natural oxygen the isotope exchange takes place mainly in the temperature range of 300–470°C (Fig. 13). The results obtained by Conder *et al.* [72] by TG for the ^{18}O isotope content of the as-synthesized sample showed good agreement with SIMS (secondary ion mass spectrometry) data.

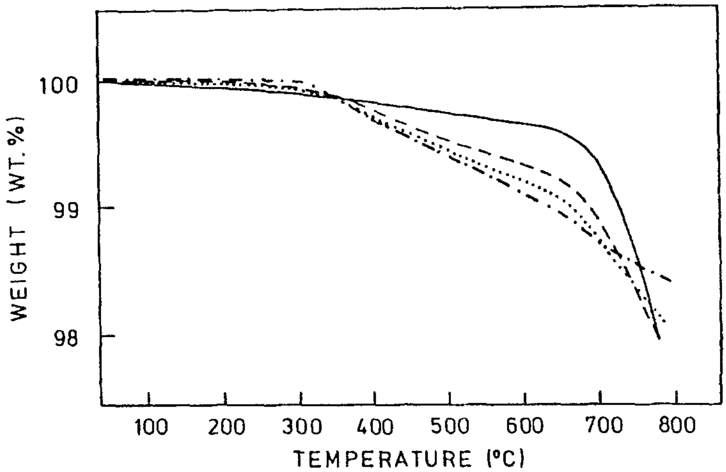

Fig. 14 Heating TG curves for $YBa_2(Cu_{1-x}Fe_x)_4O_{8-y}$ with $x=0.00$ (solid line), 0.01 (broken line), 0.03 (dotted line) and 0.04 (dotted-broken line) in Ar indicating the presence of small amounts of $YBa_2Cu_3O_{7-y}$ impurities even at very low Fe concentrations (after [74])

4.3. *Confirmation of the oxygen stability of $YBa_2Cu_4O_{8-y}$*

Because of the structural similarities, the *d* values of the strongest peaks in the XRD patterns of $YBa_2Cu_3O_{7-y}$ and $YBa_2Cu_4O_{8-y}$ coincide, which makes it difficult to distinguish between these two phases in diffraction studies [73]. In order to detect small amounts of $YBa_2Cu_3O_{7-y}$ impurities, TG measurements on the oxygen stability of various non-doped and Eu-, Ca- and Fe-doped $YBa_2Cu_4O_{8-y}$ samples have been utilized [73–76]. The $YBa_2Cu_3O_{7-y}$ structure starts to lose oxygen around 350°C (Section 2.1), while the $YBa_2Cu_4O_{8-y}$ compound is stable up to 670°C even in an inert atmosphere. In the case of $YBa_2(Cu,Fe)_4O_{8-y}$ samples, TG measurements carried out under an argon atmosphere revealed a reduction in the oxygen stability, seen as an increasing amount of mass loss at around 300°C with increasing iron substitution level (Fig. 14), much before the first impurity peaks were seen in the XRD spectra [74, 75].

4.4. *Effects of internal stresses on the oxygen stoichiometry in $(RE_{1-x}Ce_x)_2CuO_{4+y}$*

Zhu and Manthiram [77] have investigated by TG systematically the effects of internal stresses on the oxygen stoichiometry in the $(RE_{1-x}Ce_x)_2CuO_{4+y}$ system. As-synthesized $(RE_{1-x}Ce_x)_2CuO_{4+y}$ samples all have excess oxygen corresponding to $0<y\leq 0.02$. At temperatures higher than 500°C these excess oxygen atoms, occupying empty octahedral interstitial sites within the $(RE,Ce)_2O_2$ fluorite layers, along with some oxygen atoms from the tetrahedral sites of the same layer are lost. The tendency to lose oxygen was found to decrease with increasing Ce content or decreasing RE^{3+} size, due to a decreasing degree of internal stresses. The internal stresses result from the bond length mismatch between the $(RE,Ce)_2O_2$ and CuO_2 layers. With the smaller rare earth elements (e.g. Gd) an increasing electrostatic repulsion between the interstitial octahedral-site and the normal tetrahedral-site oxygen atoms forces the excess interstitial oxygen atoms to be lost at lower temperatures. In that case the total mass loss occurs in two distinct steps. On the other hand, with the larger rare earth elements (e.g. La) the mass loss occurs smoothly in one step.

5. Conclusions

Thermoanalytical methods, especially thermogravimetry, have been widely applied to solve various problems related to the oxygen stoichiometry of high T_c superconducting cuprates. Most versatile approaches and numerous studies have been published on the $YBa_2Cu_3O_{7-y}$ compound but also in the case of the other rare earth or lead cuprates TA methods have proven to be indispensable in order to learn some special features of the oxygen stoichiometry characteristics. The accuracy of a properly executed thermogravimetric determination is comparable or superior to other quantitative analytical techniques and furthermore straightforward and often less time-consuming. Finally, although the easy evaporation of bismuth, thallium and mercury somewhat restricts the applicability of thermogravimetry, interesting studies have been successfully conducted on these materials as well.

Recently a large number of superconducting cuprate families has been discovered utilizing very high oxygen pressures for the syntheses [78]. Oxygen stoichiometry studies of these new high pressure phases is a challenging topic for future research.

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