Thermochimica Acta, 174 (1991) 85–97
Elsevier Science Publishers B.V., Amsterdam

OXIDATION–REDUCTION AND OTHER GAS–SOLID REACTIONS OF HIGH-T_c SUPERCONDUCTORS

P.K. GALLAGHER

Departments of Chemistry and Materials Science & Engineering, The Ohio State University Columbus, OH 43210 (U.S.A.)

(Received 17 September 1990)

ABSTRACT

Understanding and controlling the reactions of the high-T_c superconducting oxides with their gaseous environment are critical to attaining and preserving the optimal performance of the materials and resulting devices. These important interactions fall in two general classes. The first is concerned with the reversible exchange of oxygen between the oxide and the atmosphere at temperatures above about 300 °C. These oxidation–reduction phenomena establish the oxygen content of the solid and hence its intrinsic electrical and magnetic properties. The second category concerns the reaction of the superconductor with the ambient gases to produce undesired products initially at the surface or grain boundaries, analogous to corrosion. These products, along with the overall microstructure, impurities, defects, etc., determine the effective electrical properties.

INTRODUCTION

The advent of high temperature superconducting oxides has led to renewed interest in solid state chemistry. Many of the properties of oxides, particularly the electrical and magnetic properties, are highly dependant upon the stoichiometry. Never has this been more true than in the case of some of these superconducting oxide systems, e.g. $Ba_2YCu_3O_{6-7}$. There are tremendous changes in electrical conductivity across the very wide range of oxygen content for this single phase material [1,2].

To date the high-T_c materials have been largely confined to layered cuprate systems. The changes in oxygen content require charge compensation. As oxide ions are added the compensating positive charge was initially thought of as forming some Cu^{3+} ions. More recent calculations suggest that O^- may be more probable [3,4,5]. Sleight [6] has presented a relevant discussion of this concern.

Besides the question of charge compensation there is the added consideration of the effects of point defects on the properties and reactivities of the material. There is evidence that neutron irradiation induces flux pinning sites which raise the critical current carrying capacity of the superconductor without altering the temperature of transition [7]. The former implies defect formation while the latter suggests no significant change in oxygen content. The fact that T_c does not change, however, can be the result of a continuous path of material which was not affected by the irradiation while the flux pinning sites themselves may have very local large deficiencies in oxygen content. The formation of larger numbers of oxygen vacancies by means of a more reducing atmosphere or higher temperature, however, will not only change the electrical and magnetic properties but will also markedly enhance the reactivity of the system [8,9]. This change in reactivity can have a significant effect upon the conditions of synthesis.

Clearly the exchange of oxygen between the superconductor and its environment is a very critical factor in the preparation of the materials and any devices. There are other reactions with the atmosphere, however, which are also very important. A number of investigations have pointed out the unfortunate tendency of many of these superconductors to react deleteriously with carbon dioxide and/or moisture present in the atmosphere [10,11]. Even the early stages of such reactions severely degrade the superconducting properties of the material by introducing insulating phases at the surface and at grain boundaries. Although the greater part of the sample may remain unaffected and superconducting, the surface path for conductivity at high frequencies is destroyed or the continuity through the bulk material, in the case of d.c. conductivity, is impeded by the necessity to tunnel through semiconducting or insulating grain boundaries.

Thermal analysis, particularly thermogravimetry (TG), is ideally suited to the study of many aspects of the interactions of these superconducting oxides with their gaseous environment. This brief review will highlight some of the relevant thermoanalytical investigations in this area. The enormous and rapid production of papers in this field precludes any form of exhaustive or even very comprehensive review. Consequently, only a representative selection of the literature is discussed.

OXYGEN STOICHIOMETRY

Analysis

In order to accurately follow the variation in oxygen content with temperature and partial pressure of oxygen, P_{O_2}, it is necessary to know exactly the oxygen content at some fixed point. Thereafter, it can be determined by accurately following weight changes from that reference value as the parameters of interest are varied. There are a number of analytical methods that have been successfully used to determine this initial reference value. Various physical techniques have been applied, e.g. Raman [12],

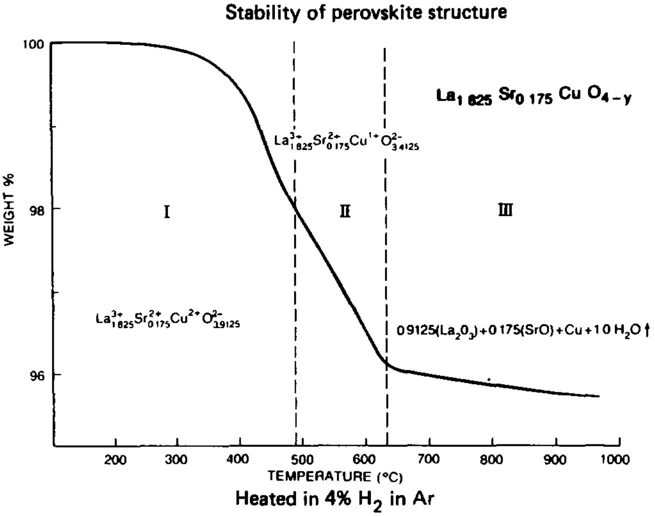

Fig. 1. Weight loss for $La_{1.825}Sr_{0.175}CuO_{4-Y}$ heated at 20 °C min^{-1} in a mixture of 4% H_2 in Ar [25].

optical [13,14], and neutron diffraction [15] methods. Chemical methods have involved iodometric [16,17], dichromate [18] redox titrations and electrochemical [19,20] schemes.

TG in reducing atmospheres has been used successfully in studies of closely related catalytic compounds, e.g. $BaPtO_3$ [21] and alkali metal substituted rare earth manganates [22] or cuprates [23]. As the importance of the oxygen content in superconductors became apparent it was logical to extend the analytical method to this application [2,23,24]. Examples of the method are presented in Fig. 1 for $La_{1.825}Sr_{0.175}CuO_{4-y}$ [25], in Fig. 2 for $Ba_2YCu_3O_{7-x}$ [24], and in Fig. 3 for Pb $Sr_2YCu_3O_{8.00}$ [26]. In each case the final products are the alkaline and rare earth oxides and metallic copper and lead. From the observed weight loss and the final composition it is a simple

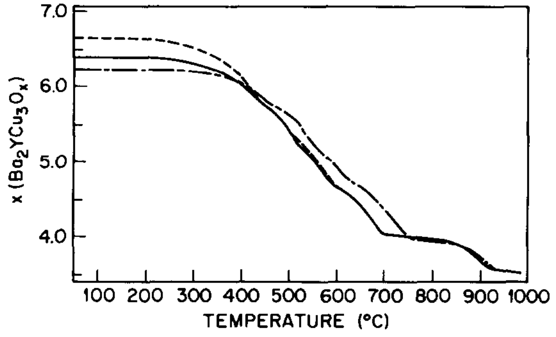

Fig. 2. TG curves at 10 °C min^{-1} in 15% H_2 in N_2 for the reduction of $Ba_2YCu_3O_X$ prepared by low temperature oxidation of powder with $X = 6.70$, 6.44, and 6.28 [24].

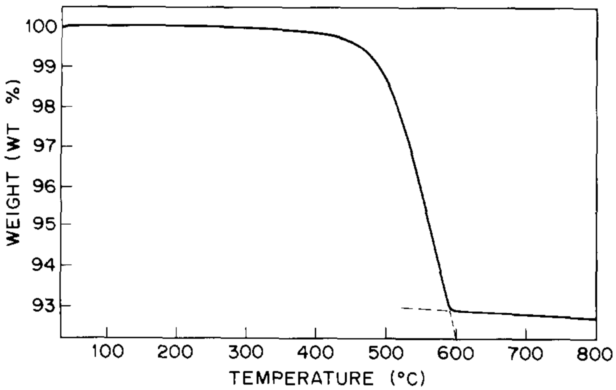

Fig. 3. TG curve for $Pb_2Sr_2YCu_3O_{8.0}$ at 10°C min^{-1} in 15% H_2/85% N_2 [26].

process to calculate the oxygen content of the original sample. The primary inherent limitation of this method concerns the volatility of the metals in reducing atmospheres [25,26]. This has prevented the application of this method to the bismuth-containing systems [27].

Because the weight losses are not great, it is advisable to subtract blank runs made under nearly identical conditions in order to alleviate the uncertainties associated with buoyancy and the aerodynamic or convective forces. In addition the accuracy is highly dependent upon the absence of even relatively small amounts of second phases [28]. The maximum oxygen content for single phase $Ba_2YCu_3O_7$ material seems to be 7.00 [2] although slightly higher values, round 7.03, have been observed for samples treated at high values of P_{O_2} [28].

Variation with temperature and P_{O_2}

Once the oxygen content of a sample has been established it is then feasible to follow how that oxygen content varies as a function of temperature and P_{O_2}. Electrochemical cells have been used for this purpose [29] but careful TG represents the most convenient method for following the changes in oxygen content as these parameters are changed. The most accurate data is obtained by making isothermal steps and allowing the sample to come to constant weight. By doing this in both heating and cooling patterns it is possible to establish that the same weight is achieved coming from both directions. This strongly suggests that equilibrium conditions prevail. By following the weight change which occurs and applying the appropriate corrections for changes in buoyancy and aerodynamic forces it is possible to determine the oxygen content of the material. There have been extensive studies of the $Ba_2YCu_3O_{7-x}$ system by this method, summarized and reviewed by Lindemer et al. [30].

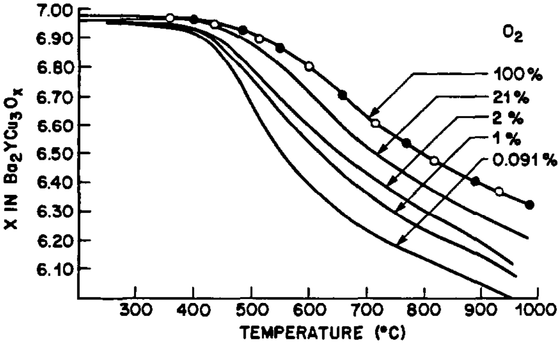

Fig. 4. TG curves for $Ba_2Cu_3O_{6\ 98}$ heated at 1° C min^{-1} in flowing atmospheres. Points shown are for isothermal experiments, open on heating and closed on cooling [23].

It is also possible to achieve satisfactory data by dynamic TG provided that the kinetics are favorable. Figure 4 is an example of conventional TG curves made at 1° C min^{-1} in the indicated atmospheres [23]. These data are for ground powders which favor a relatively high rate of oxidation. The cooling curve in oxygen retraces the heating, and isothermal points indicated by the circles fall nicely on the curve. However, as was pointed out at the time of the measurements [23,31] and in greater detail later [30], this rate of approach to equilibrium decreased with decreasing P_{O_2} as well as with temperature. The kinetics of this oxidation–reduction process are interesting [32] and are described later in this volume along with the fascinating thermal expansion of these high-T_c superconductors.

The TG-based data on oxygen stoichiometry for $Ba_2YCu_3O_{7-x}$ are nicely summarized in Fig. 5 (from Lindemer et al. [30]). The equilibrium value of x is shown as a function of temperature and P_{O_2}. The orthorhombic-to-tetragonal phase transition is indicated by the dashed line based on the data of Specht et al. [33]. Since the high temperature superconductivity has been clearly shown to depend upon a high oxygen content ($x < 0.15$), the need for a low temperature anneal is obvious. At conditions of formation and sintering ($T > 800$ ° C) impractically high oxygen pressures would be necessary to achieve the necessary oxygen content. This low temperature anneal can be accomplished using oxidizing agents other than the conventional molecular oxygen. Plasma enhanced oxidation has been shown to be effective [34].

The change in oxygen content with P_{O_2} will markedly change the vacancy content of the material at constant temperature. Such changes influence a variety of properties. The pronounced decrease in melting point with lowered oxygen content is seen in Fig. 6 [23]. The chemical reactivity may also be altered, increasing with increasing vacancy content. This has been demonstrated fr the formation reaction based upon the reaction of $BaCO_3$ with Y_2O_3 and CuO [8,9].

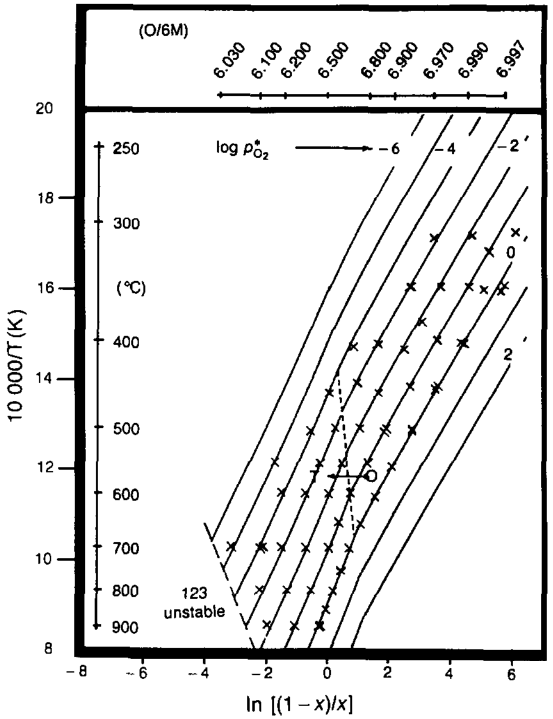

Fig. 5. Oxygen content, X, as a function of temperature and P_{O_2} for $Ba_2YCu_3O_X$ [30]. Dashed line is for the orthorhombic-to-tetragonal transition [33].

Similarly the electrical conductivity varies greatly and undergoes a metallic-to-semiconducting transformation as the oxygen content drops below about 6.25. This is evident in Fig. 7 [35]. The conductivity also undergoes a slight change as it passes through the orthorhombic-to-tetragonal transformation. This slight change is best detected from the differential of the resistance change with respect to temperature [36]. The resistivity of

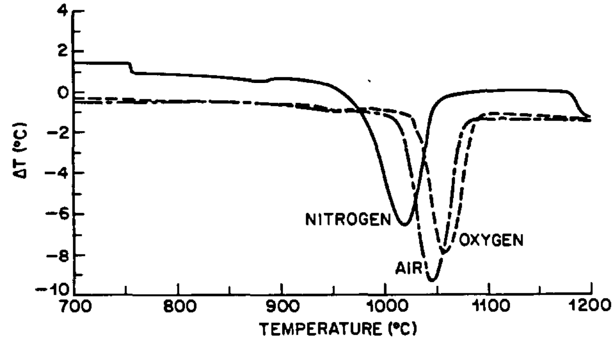

Fig. 6. DTA curves for 150 mg of $Ba_2YCu_3O_7$ heated at 20 °C min^{-1} in the indicated flowing atmospheres [23].

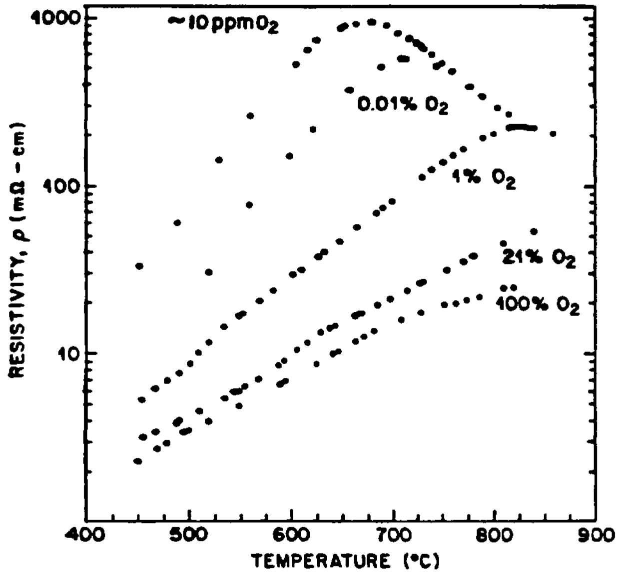

Fig. 7. Electrical resistivity of $Ba_2YCu_3O_x$ as a function of temperature in the indicated flowing atmospheres [35].

the material appears to be dependent only upon the oxygen content, regardless of how that content is achieved, and consequently may serve as a relatively simple analytical or quality control method [35].

Solution calorimetry has also been used to investigate the thermodynamic nature of these oxygen vacancies. Dissolution in perchloric acid at slightly elevated temperatures has been used to determine the heat of formation of the compound with varying oxygen content [37]. Also, molten salts have been used at higher temperatures to evaluate thermodynamic quantities as a function of oxygen content [38]. Calorimetric measurements of the enthalpy of oxidation and of the orthorhombic-to-tetragonal transition have also been made [39].

The preceding discussion has dealt primarily with the 123 composition; however, the 124 composition is also superconducting and with suitable partial substitutions its transition temperature can approach that of the 123 compound [40]. The 124 compound has a much smaller oxygen weight loss below about 800 °C and therefore has generated interest as a potentially more viable system for encapsulation, etc [41]. There is, however, recent evidence to suggest that these small weight losses below 800 °C do significantly influence the superconducting properties [42]. The 124 compound decomposes at atmospheric pressure above about 800 °C with the precipitation of CuO to form the 123 compound [41,43].

Although there has also been a large body of work generated on the bismuth- and thallium-based superconducting systems, the effort devoted to oxygen content has not been nearly as extensive as for the barium–rare

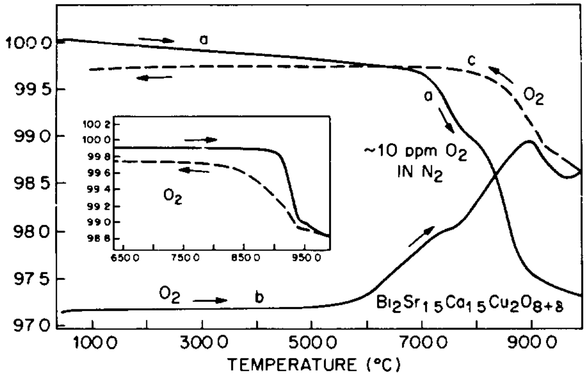

Fig. 8. TG curves for $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_{8+\delta}$ heated at 2°C min^{-1} in the indicated flowing atmospheres [27].

earth–copper systems. The range of single phase oxygen content is less and the low temperature weight loss is much smaller [27]. The TG curves of $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_{8+\delta}$ heated at 2°C min^{-1} in oxygen and nitrogen are shown as an example in Fig. 8. The material does not loose much weight until the melting point. As in the case of the 124 compound described earlier, there is evidence that the small amount of reversible oxygen loss, shown in Fig. 9, does alter the superconducting transition temperature [44,45,46]. The melting point of these materials is dependent on the P_{O_2} (see Fig. 10), similar to the behavior of the 123 superconductor [27].

The greatest variations in the range of oxygen content for single phase materials is observed in the $Pb_2Sr_2Ln_{1-x}M_xCu_3O_{8+z}$ system [47,48]. Behavior in this system contrasts strongly with that observed in the 123 system in that optimal superconducting behavior is achieved at the low end of the range of oxygen contents, i.e. in the relatively reduced range with small values of z [49]. Samples which have exhibited the highest superconducting

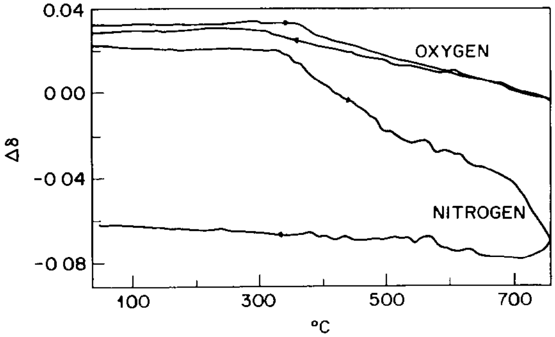

Fig. 9. TG curves of $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_{8+\delta}$ heated at 4°C min^{-1} in the indicated flowing atmospheres [44].

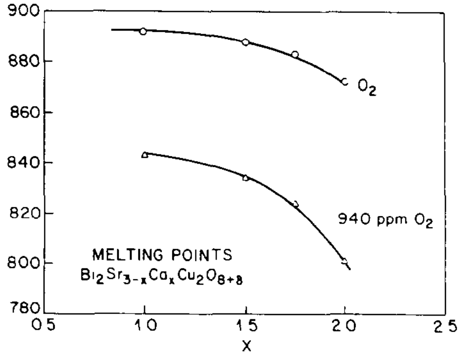

Fig. 10. Melting points of $Bi_2Sr_{3-X}Ca_XCu_2O_{8+\delta}$ as determined by DTA in the indicated flowing atmospheres [27].

temperatures in the system are where yttrium is the lanthanide, M is calcium and x is the apparent upper limit of solubility, 0.4. TG curves for this material heated at 2° C min^{-1} in various atmospheres are presented in Fig. 11 [26].

The optimum superconducting properties are achieved when the oxygen content is essentially 8.0. The structure is orthorhombic at that point. As the material is heated it takes up very large quantities of oxygen and transforms to a semiconducting tetragonal modification. The contrast with the behavior of the 123 is striking in that the 123 looses oxygen on heating as it goes to the semiconducting tetragonal modification. In addition, the thermal expansion behavior is completely different in the two systems as shown in a following review by O'Bryan.

At temperatures beyond 500–600° C the compound loses oxygen and tends to reform the orthorhombic superconducting form depending upon the P_{O_2}. As the temperature and P_{O_2} increase the compound undergoes oxidative decomposition. The Pb is oxidized and a second phase forms having a pseudocubic perovskite structure. At still higher temperatures the Pb reduces

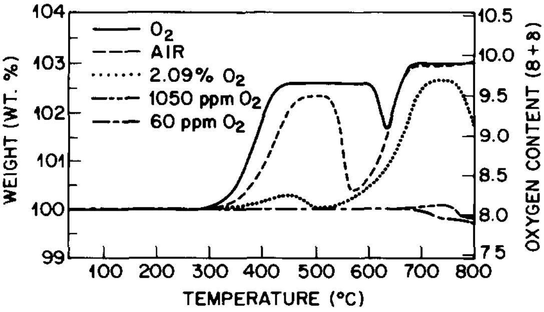

Fig. 11. TG curves for $Pb_2Sr_2Y_{0.60}Ca_{0.40}Cu_3O_{8.08}$ heated at 2° C min^{-1} in the indicated flowing atmospheres [26].

and the superconducting orthorhombic phase reforms. These represent the general conditions for synthesis of the superconducting phase but the material must be cooled back to room temperature in a low P_{O_2} environment in order to prevent undesirable oxidation in the 300–600 °C range. The relationship between oxygen content and superconductivity for this lead-based system suggests *n*-type behavior similar to that observed in the $Nd_{2-x}Ce_xCuO_y$ system [50]. In this latter system only a small amount of oxygen is lost at temperatures above 800 °C. The oxygen loss is not entirely reversible and some decomposition is necessary in order to attain a sufficiently reduced state for superconductivity. Unlike the 123 material both the Pb-based system and the *n*-type material can be readily deactivated by normal oxidation.

GAS-SOLID REACTIONS

It was noted very early in the study of these highly oxidized cuprate materials that they are unstable after exposure to moisture; in fact, the orthorhombic 123 phase reacts directly with liquid water at room temperature to liberate oxygen [10]. The long-term exposure of the material to high humidity degrades the electrical performance, presumably as a result of both reduction and the formation of insulating hydroxides on the surface and grain boundaries. A TG curve for the 123 compound is shown in Fig. 12 when heated at 1 °C min^{-1} in wet and dry oxygen. The weight loss in the dry gas is as would be predicted from Fig. 4; however, there is an initial weight gain in the moist atmosphere [11].

The superconducting properties of the sample were studied during this heating process and found to immediately degrade simultaneously with the weight gain. When the sample was heated to temperatures where the most stable hydroxide, $Ba(OH)_2$ decomposes, the weight changes in wet or dry

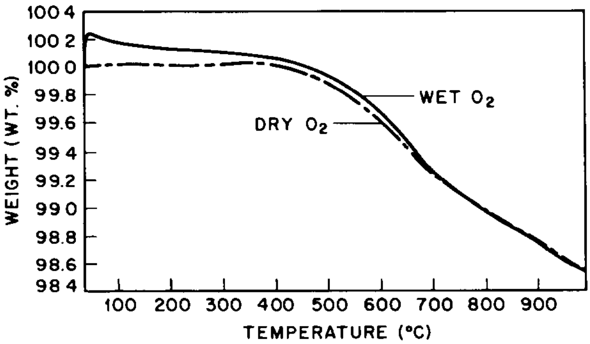

Fig. 12. TG curves for $Ba_2YCu_3O_{6.98}$ in flowing wet and dry O_2 at 1 °C min^{-1} [11]. (— — —), dry O_2, 361 mg; (———), O_2 saturated with H_2O at 23 °C, 287 mg.

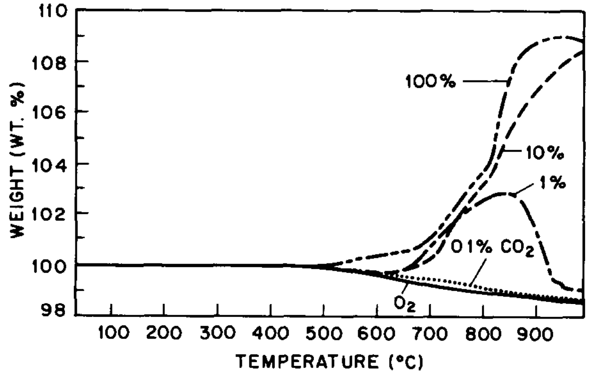

Fig. 13. TG curves for $Ba_2YCu_3O_{6.98}$ in the indicated flowing atmospheres at 2 °C min^{-1} [11]. (———), 100% O_2, 274 mg; (······), 0.1% CO_2, in O_2, 233 mg; (— — —), 1% CO_2, in O_2, 256 mg; (- - - - -), 10% CO_2, in O_2, 244 mg; (·—·—·), 100% CO_2, 293 mg.

atmospheres were identical. If a sample which is degraded by heating in a moist atmosphere is heated above 600 °C and then cooled in a dry atmosphere it will become superconducting again provided that the necessary oxygen content has been restored by an appropriate low temperature anneal.

The reaction of CO_2 with the 123 material is an even greater problem. TG curves for heating 123 powder at 2 °C min^{-1} in various concentrations of CO_2 are shown in Fig. 13 [11]. Even at the level of 0.01% there is a departure from the normal weight loss curve of the sample. Measurements of the superconducting properties, however, show severe degradation long before a perceptible weight gain occurs. The curves for higher concentrations of CO_2 indicate a total breakdown of the 123 material at elevated temperatures to essentially reform $BaCO_3$ analogous to a reverse synthesis process. If the P_{CO_2} is lowered then the $BaCO_3$ will readily react again as in the normal synthetic process to regenerate 123 material.

There are several corrosive oxidizing agents which could combine the positive attribute of enhancing the oxygen content of a 123 specimen, thereby enhancing its superconducting properties, with the negative aspect of reaction to form undesireable insulating surface and grain boundary films. Examples of this are higher oxides of nitrogen which could form nitrates simultaneous with the elimination of oxygen vacancies. Thermal analysis, particularly TG and evolved gas analysis, can again play a prominent role in understanding these complex heterogeneous processes.

SUMMARY

It is hoped that the information presented here has demonstrated the crucial role that the oxygen stoichiometry has in the superconducting properties of these fascinating cuprates. The ranges of oxygen nonstoichiometry vary considerably, but the 123- and Pb-based systems have an enormous reversible range of oxygen content while still preserving the single phase structure. The transformation from orthorhombic to tetragonal symmetry occurs as oxygen is removed from the 123 material or as oxygen is added to the Pb-based system. In both cases it is the orthorhombic form that has the desired superconducting properties. Although the oxygen variations are much smaller in the other superconducting systems, they nevertheless significantly influence the superconducting transformation temperature.

Thermoanalytical methods are particularly useful to (1) analyse the initial oxygen content of a sample by means of reduction by hydrogen to a well-defined state; (2) follow the changes in oxygen stoichiometry and melting point as such important parameters as temperature and P_{O_2} are varied; and (3) study the reactions of the superconductor with other gases, e.g. H_2O or CO_2, in the environment, which generally lead to a degradation of the superconducting properties. The use of thermal analysis to study other vital aspects of these interesting materials is described in the companion reviews in this special volume of Thermochimica Acta.

REFERENCES

1 R.J. Cava, B. Battlogg, C.H. Chen, E.A. Reitman, S.M. Zahurak and D. Werdner, Phys. Rev. B, 57 (1987) 5719.
2 P.K. Gallagher, H.M. O'Bryan, S.A. Sunshine and D.W. Murphy, Mater. Res. Bull., 22 (1987) 995.
3 J.M. Tranquada, S.M. Heald and A.R. Moodenbaugh, Phys. Rev. B, 36 (1987) 5263.
4 C.N.R. Rao, P. Ganguly, M.S. Hedge and D.D. Sharma, J. Am. Chem. Soc., 109 (1987) 6893.
5 N. Nucker, J. Fink, J.C. Fuggle, P.J. Durhamand and W.M. Temmermann, Phys. Rev. B, 37 (1988) 5158.
6 A. Sleight, Science, 242 (1988) 1519.
7 R.B. van Dover, E.M. Gyorgy, L.F. Schneemeyer, J.W. Mitchell, K.V. Rao, R. Puzniak and JV. Wasczak, Nature, 342 (1989) 342.
8 P.K. Gallagher and D.A. Fleming, Chem. Mater., 1 (1989) 659.
9 G.S. Grader, P.K. Gallagher and D.A. Fleming, Chem. Mater., 1 (1989) 665.
10 M.F. Yan, R.L. Barnes, H.M. O'Bryan, P.K. Gallagher, R.C. Sherwood and S. Jin, Appl. Phys. Lett., 51 (1987) 532.
11 P.K. Gallagher, G.S. Grader and H.M. O'Bryan, Mater. Res. Bull., 23 (1988) 1491.
12 M. Hangyo, S. Nakashima, K. Mizoguchi, A. Fujii and A. Mitsuishi, Solid State Commun., 65 (1988) 835.
13 E.T. Johnson and J.W. Mitchell, Anal. Chemica. Acta, 217 (1989) 5360.
14 M.K. Kelley, S-W. Chan, K. Jenkin, D.E. Aspenes, P. Barboux and J-M. Tarascon, Appl. Phys. Lett., 53 (1988) 2333.
15 W.I.F. David, Nature, 327 (1987) 310.
16 D.C. Harris and T.A. Hewston, J. Solid State Chem., 69 (1987) 182.
17 A.I. Nazzal, V.Y. Lee, R.D. Jackowitz, Y. Tokura and J.B. Torrance, Physica C, 153–155 (1988) 1367.
18 J-M. Tarascon and B. Bagley, Mater. Res. Soc. Bull., 14 (1989).

19 J.M. Rosamilla and B. Miller, Anal. Chem., 61 (1989) 1497.
20 G. Kawamura and M. Hiratani, J. Electrochem. Soc., (1987) 3211.
21 P.K. Gallagher, D.W. Johnson, E.M. Vogel, G.K. Wertheim and F.J. Schnettler, J. Solid State Chem., 21 (1977) 277.
22 E.M. Vogel, D.W. Johnson and P.K. Gallagher, J. Am. Ceram. Soc., 60 (1977) 31.
23 P.K. Gallagher, Adv. Ceram. Mater., 2 (1987) 632.
24 P.K. Gallagher, H.M. O'Bryan and G.S. Grader, Thermochim. Acta, 137 (1989) 373.
25 E.M. Vogel, G.W. Hull and J-M. Tarascon, Mater. Lett., 6 (1988) 269.
26 P.K. Gallagher, H.M. O'Bryan, R.J. Cava, A.C.W.P. James, D.W. Murphy, W.W. Rhodes, J.J. Krajewski, W.F. Peck and J. Wasczak, Chem. Mater., 1 (1989) 277.
27 G.S. Grader, E.M. Gyorgy, P.K. Gallagher, H.M. O'Bryan, D.W. Johnson, S.A. Sunshine, S.M. Zahurak, S. Jin and R.C. Sherwood, Phys. Rev. B, 38 (1988) 757.
28 H.M. O'Bryan, P.K. Gallagher, R.A. Laudise, A.J. Caporaso and R.C. Sherwood, J. Am. Ceram, Soc., 72 (1989) 1298.
29 M. Tetenbaum, in Ceramic Superconductors II, M.F. Yan (Ed.), Am. Ceram. Soc., Westerville, OH, 1988, pp. 51–58.
30 T.B. Lindemer, J.F. Hunley, J.E. Gates, A.L. Sutton, J. Brynestad, C.R. Hubbard and P.K. Gallagher, J. Am. Ceram. Soc., 72 (1989) 1775.
31 H.M. O'Bryan and P.K. Gallagher, Adv. Ceram. Mater., 2 (1987) 642.
32 H.M. O'Bryan and P.K. Gallagher, J. Mater. Res., 3 (1988) 619.
33 E.D. Specht, C.J. Sparks, A.G. Dhere, J. Brynestad, O.B. Cavin, D.M. Kroger and H.A. Oye, Phys. Rev. B, 37 (1988) 7426.
34 B.G. Bagley, L.H. Greene, J-M. Tarascon and G.W. Hull, Appl. Phys. Lett., 51 (1987) 622.
35 G.S. Grader, P.K. Gallagher and E.M. Gyorgy, Appl. Phys. Lett., 51 (1987) 1115.
36 A.T. Fiore, M. Gurivitch, R.J. Cava and G.P. Espinosa, Phys. Rev. B, 36 (1987) 7262.
37 L.R. Morss, D.C. Sonnenberger and R.J. Thorn, Inorg. Chem., 27 (1988) 2106.
38 A. Navrotsky, in Proc. Conf. Chem. Elect. Ceram., R. Roth (Ed.), Jackson Hole, WY, Aug. 1990, NIST.
39 B.E. Vigeland and S. Julsrad, Physica C, 162–164 (1989) 546.
40 T. Miyatake, S. Gotoh, N. Koshizuka and S. Tanaka, Nature, 341 (1989) 41.
41 S. Jin, H.M. O'Bryan, P.K. Gallagher, T.H. Tiefel, R.J. Cava, R.A. Fastnacht and G.W. Kammlott, Physica C, 165 (1990) 415.
42 J.E. Graebner, H.M. O'Bryan, R.A. Fastnacht and S. Jin, Physica C, in press.
43 J. Karpinski, E. Kaldis, E. Jilek, S. Rusiecki and B. Bucher, Nature, 336 (1988) 660.
44 H.M. O'Bryan, W.W. Rhodes and P.K. Gallagher, Chem. Mater., 2 (1990) 421.
45 R.G. Buckley, J.L. Tallon, J.W.M. Brown, M.R. Presland, N.E. Flower, P.W. Gilberd, M. Bowden and N.B. Milestone, Physica C, 156 (1988) 629.
46 D.E. Morris, C.T. Hultgren, A.M. Markelz, J.Y.T. Wei, N.G. Asmar and J.H. Nickel, Phys. Rev. B, 39 (1989) 6612.
47 R.J. Cava, B. Batlogg, J.J. Krajewski, L.W. Rupp, L.F. Schneemeyer, T. Siegcrist, R.B. van Dover, P. Marsh, W.F. Peck, P.K. Gallagher, S.H. Glarum, J.H. Marshall, R.C. Farrow, J.V. Waszchak, R. Hull and P. Trevor, Nature, 336 (1988) 211.
48 M.A. Subramanian, Physica C, 157 (1987) 124.
49 E.M. Gyorgy, H.M. O'Bryan and P.K. Gallagher, Chem. Mater., 1 (1989) 571.
50 J-M. Tarascon, E. Wang, L.H. Greene, B.G. Bagley, G.W. Hull, S.M. D'Egido, P.F. Miceli, Z.Z. Wang, T.W. Jing, J. Clayhold, D. Brawner and N.P. Ong, Phys. Rev. B, 40 (1989) 4494.