Journal of Thermal Analysis, Vol. 48 (1997) 585-596

DTA/TG COUPLING
Applications in the field of superconducting materials with high critical temperature

J. L. Jorda

Univ. Savoie, L. S. M, 9 rue de l'arc-en-ciel, BP240, F-74942 Annecy Le Vieux, France

Abstract

With the discovery of high temperature superconductivity an extraordinary field for investigations on new materials containing up to (more than) 8 or 9 components has been open. But, in addition to problems specifically related to superconductivity, we are faced with a prelimary difficulty: the preparation of well defined compounds which may have reproducible properties. This difficulty is smoothed out when the phase relations in the relevant systems are known. Differential Thermal Analysis (DTA) contributes to their establishment. However, in multicomponent systems, an isopletic line is expected to intercept various boundary surfaces and the analysis is obviously complicated, compared to low order systems. In addition, by the nature of high temperature superconductors the oxygen partial pressure used for their preparation is an important thermodynamic parameter which contributes to fix the oxygen content in the solid state. During heat treatments, the composition of the systems may change, due to oxygen or volatile oxides (Tl_2O_3, PbO_2 or HgO) release. A permanent composition control then requires thermogravimetric (TG) measurements associated to DTA.

This paper attempts to demonstrate the efficiency of the assembly DTA/TG for the study of high temperature superconductors. Going beyond the frame of preparation and quality control, the system is also particularly useful for kinetic studies. Examples will be principally in the (Tl,Pb)–(Ba,Sr)–Ca–Cu–O systems.

Keywords: DTA, high temperature superconductors, phase diagrams, TG, thermal analysis

Introduction

The driving force for the quantitative study of equilibrium diagrams of condensed phases is the optimization of the properties of materials. It has to be associated with the development of thermal methods of analysis. In a recent review, Prince [1] traced back the birth of Thermal Analysis of alloys in 1829 in a contribution by Rudberg and Svenska [2] concerning the determination of the eutectic temperature in the Sn–Pb system. Seventy years later, Austen [3] in order to improve the efficiency of steel production, conceived the first differential thermal analyser and published the first DTA curve obtained on cooling "electro-iron" using Pt/Pt-10% Ir thermocouples. Thermogravimetry is due to Honda [4] who performed the first simultaneous measurement of weight change during temperature evolution. Coupling DTA/TG is a more recent expansion initiated in the sixten's.

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

Equilibrium phase diagrams of superconducting systems

The relation between phase equilibrium diagram and superconducting properties was originated by the determinent influence of thermal treatment on the critical temperature T_c of some A15 phases [5, 6].

Conventional superconductors

Ten years ago, the most promising superconducting materials for applications could be classified in two families: the A15 compounds of general formulae T_3B (T=Nb, V; B=Ga, Ge, Al..) with $T_c \cong 20$ K and Chevrel phases with high critical field H_{c2} corresponding to MMo_6X_8 (M=Cu, Pb; X=S, Se).

In the former series, T_c was found to be critically dependent on the composition as shown in Fig. 1 for the systems $Nb_{1-\beta}B_\beta$ [7]. The ratio T_c to the maximum critical temperatures T_{cm} measured in the relevant compounds was established after a careful investigation of the homogeneity range of the A15 phases at temperatures in the range of 2000°C and was found to be linear with β. The actual difficulty was to perform thermal analysis at such high temperatures. The use of high refractory oxides (BeO, ZrO_2) crucibles and W/W-Re thermocouples in DTA cells as well as the de-

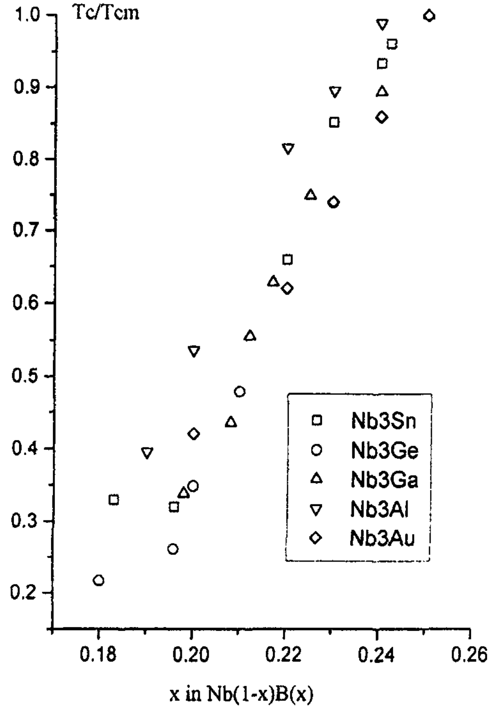

Fig. 1 Relation of the normalized superconducting temperature T_c/T_{cm} and the composition in some Nb-based A15 phases. T_{cm} is the maximum critical temperature found in the relevant systems: Nb_3Al(19.1 K), Nb_3Ga(20.7 K), Nb_3Ge(23 K), Nb_3Au(11.5 K) and Nb_3Sn(18 K)

velopment of new methods such as thermal analysis on levitating samples solved the problem [7, 8].

For the chalcogenides, similar behaviour on $T_c(x)$ may be observed as pointed out by Johnston *et al.* [9] for $Cu_xMo_6S_8$. The phase diagram under an argon pressure of 1 kbar [10] confirmed the strong dependence of the phase limits with the temperature. The high pressure used for the preparation of homogeneous samples avoided eventual compositional changes due to sulfur mobility but indeed, the system foreshadowed the problems encountered at present for the study of High Temperature Superconductors.

High Temperature Supercorductors (HTSC)

For cuprate superconductors, due to the bidimensional character of the structure, cationic substitution may have different effect on T_c, depending on the layer which is concerned. It may be dramatic if the CuO_2, or an adjacent plane influencing on the carrier concentration is affected. Inversely, poor effects are generally observed in series where the substituted atoms belongs to the same family, in the limit of stability of the phase. An example is shown in Fig. 2 for the $(Tl_{0.5}Pb_{0.5})Sr_{2-x}Ba_xCa_2Cu_3O_z$ system [11] for which the Ba substitution for Sr in the equilibrium solid solution field ($x \leq 0.4$) yields to a change of T_c restricted to 2 K. This figure also reveals, for a given x value ($x=0.2$) a more important contribution to T_c due to the path for the phase formation which strongly depends on the thermodynamic properties of the components and intermediate compounds. Again, the role of the phase diagram emerges but the study is complicated by additional parameters to temperature.

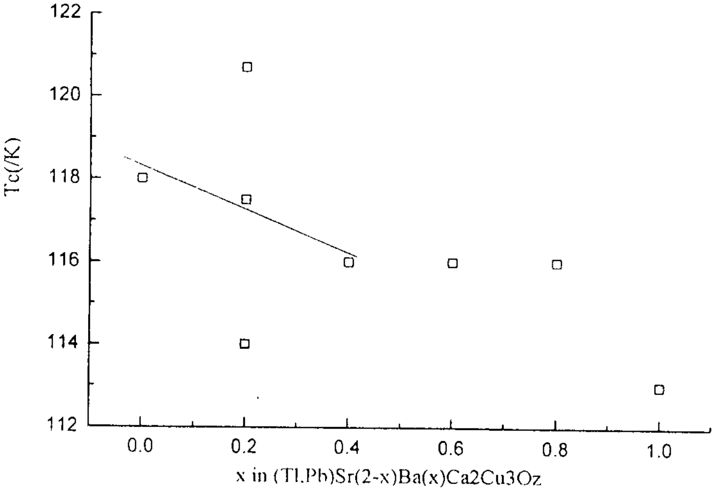

Fig. 2 T_c(K) as a function of the rate x of Ba substitution in the high T_c superconductor $(Tl_{0.5}Pb_{0.5})Sr_{2-x}Ba_xCa_2Cu_3O_z$. Samples with $x<0.4$ are nearly single phase. For $x=0.2$ a maximum deviation (7 K) for T_c is observed for different heat treatments

The number of components, up to 9, which enters into the composition of the superconducting cuprates is a problem for geometrical representation. One of the interest of the phase diagram drawings is the possibility it offers to visualize a path for solidification and to define a field of formation of the compounds. Ternary systems at constant pressure are the upper limit for easy representation of isothermal sections. For higher order systems solutions have been proposed using either a geometrical approach consisting to reduce the dimension of the system [12] or vectorial methods which may be adapted to microcomputers [13]. However none of these methods are actually efficient for experimental optimization and for instance, to determine the composition of a quaternary eutectic for which the 4 ternary eutectics have to be first localized, at least 48 experiments are necessary [14]! Computer modeling will be of great interest when the thermodynamic quantities will be available.

The oxygen content in high T_c superconductors is one of the critical parameters, influencing the structure type and/or the transition temperature. The results for $Tl_2Ba_2Cu_{6+\delta}$ are summarized in a temperature of anneal – partial oxygen pressure diagram in Fig. 3 [15]. In both orthorhombic type and tetragonal type structures which are formed in the system, the transition temperature may be changed from 0 to 90 K. Similar effects have been observed in $YBa_2Cu_3O_{7-\delta}$ [16] and the Bi-series [17, 18].

The experimental conditions for preparing HTSC not only influence the oxygen concentration but involves in many cases volatile oxides: Tl_2O_3, PbO_2, HgO... As a consequence, the control of the composition implies systematic measurements of the weight of the samples, thus justifying the use of simultaneous thermogravimetry during thermal analysis.

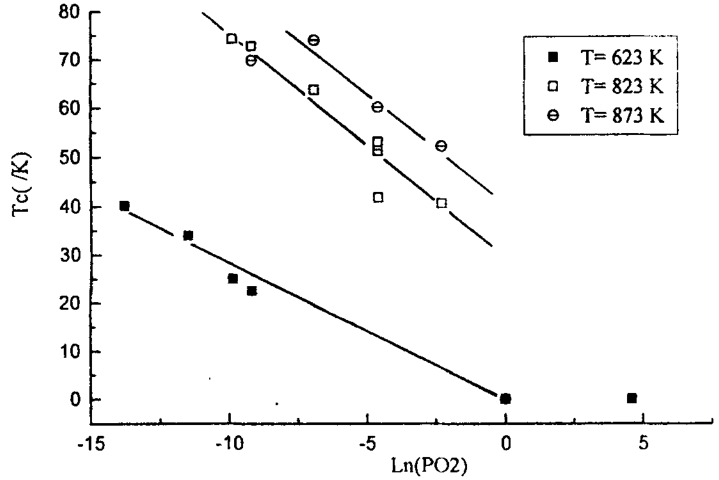

Fig. 3 Critical temperature T_c as a function of $P(O_2)$ for Tl-2201 with both orthorhombic and tetragonal type structure for annealing temperatures T=623, 823 and 873 K. From reference [15]

Caracterization of the components

The expected ultimate state of the superconducting samples should be an equilibrium state, not changing with the time at fixed thermodynamic variables (composition, pressure, temperature). Establishing equilibrium however depends on the starting components which forces a reacting path. Then it is of great importance to know their behaviour under various temperature and pressure conditions

Alkaline earths

Due to the reactivity of the alkaline earth oxides with the air humidity, Ca, Sr, and Ba are usually introduced in HTSC as nitrates, carbonates or peroxides whose decomposition has to be ascertained during direct reaction. Incomplete decomposition may result in the formation of new materials with, for instance, intercalated CO_2 [19–21].

A particular attention was paid to barium introduced in the HTSC using the peroxide BaO_2. It was found that the formation of BaO by decomposition of the peroxide in $P(O_2)=1$ bar or in oxygen flowing occurs at high temperature, through intermediate states implying the formation of suboxides BaO_{1+x} [22, 23]. A thermal analysis of BaO_2 under oxygen flowing with a heating rate of 10°C min^{-1} (Fig. 4) shows that the decomposition reaction $BaO_2 \rightarrow BaO + 1/2O_2$ is complete at 1100°C.

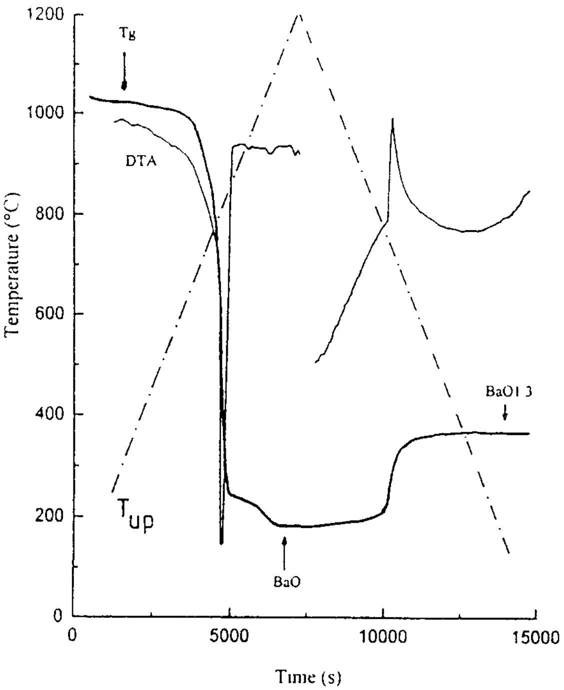

Fig. 4 DTA/TG of BaO_2 in oxygen flowing. Intermediate BaO_{1+x} compounds are reversibly formed. $BaO_{1.3}$ appears to be a metastable phase in the BaO_2–BaO system

The transient suboxide $BaO_{1.3}$ has been clearly identified by X-ray diffraction after a quench from 900°C. The crystal structure, not yet solved could be of the orthorhombic-type with $a=9.222$ Å, $b=7.20$ Å and $c=5.416$ Å and could originate from an ordered distribution of molecular oxygen in the BaO cell.

The metal oxides

A thermodynamic analysis of Cu–O has been reviewed by Schmid [24] with an associated solution model for the liquid phase. The deduced phase diagram indicates that under a pressure of 1 atm of oxygen, CuO is a stable phase up to 1130°C.

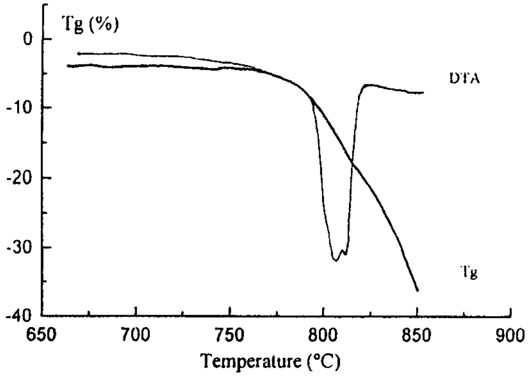

Fig. 5 DTA and TG curves for the decomposition of Tl_2O_3 in oxygen flowing. Heating rate: 10°C mn^{-1}

This temperature is decreased down to 850°C in argon but operating in such conditions is not usual to form the cuprate superconductors, excepted $Nd_{2-x}Ce_xCuO_4$ where $NdCuO_2$ was found as impurity after annealing the superconducting phase [25]. The problems with the metal oxides will arise with volatile components such as thallium oxide. Based on vapour pressure measurements, Holstein [26] reported that Tl_2O_3 in oxygen, decomposes to Tl_4O_3 at a temperature near 1073 K. Figure 5 represents a DTA/TG of Tl_2O_3 in oxygen flowing [23]. Two different rates for weight losses are observed. From 1063 K to 1095 K a first endotherm is accompanied by 8% weight losses which is more than the expected value according to the reaction $4/3Tl_2O_3(s)=2/3Tl_4O_3(s)+O_2$ but partial decomposition of Tl_4O_3 cannot be excluded and may explain this discrepancy. The second endotherm at 1095 K corresponds to the formation of a liquid phase TlO_x which readily decomposes. The behaviour of Tl_2O_3 is not a unique example which may affect the preparation of high temperature superconductors. Similar problems are encountered with PbO_2 and more critically with HgO based materials.

Phase diagrams and elaboration processes

Obviously the control of the composition is the first requirement for phase diagram determination. In closed systems with an appropriate pressure, the bulk composition is not expected to change during heating. But DTA is not yet frequently adapted to such arrangements and most of the phase equilibrium diagrams of HTSC are studied in air or limited (a few atm) oxygen partial pressure. Hence, the abstraction of composition control may have dramatic consequence. An example taken in the binary system $TlO_{1.5}$–BaO shows the evolution of the molar fraction of BaO as a function of the temperature due to thallium oxide departure (Fig. 6). Without the help of TG, the thermal response of DTA cannot be attributed to a defined equilibrium reaction.

Taking advantage of the high volatility of Tl_2O_3, we proposed an isothermal analysis [23] which was of great help to identify $Tl_6B_4O_{13}$ and $Tl_2Ba_4O_7$, compounds in the binary system $TlO_{1.5}$–BaO. While operating in gas flowing, at a given temperature, the equilibrium partial pressure of a volatile component will never be obtained and the composition continuously evoluates, crossing various equilibrium fields, as far as a stable compound at the proposed temperature is encountered. If the kinetics for decomposition is supposed to be described by a Johnson-Mehl relation: $\mathrm{Ln}(1-r)=(kt)^n$ r=fraction of decomposed phase, t=time, k and n not dependending on t, and if the size of the sample is small enough to assume nearly homogeneous composition in the bulk, we may attribute each discontinuity of the rate of

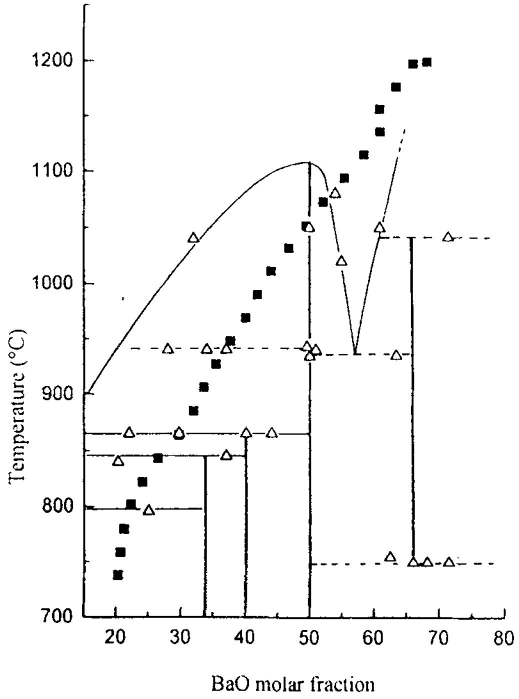

Fig. 6 Compositional change with the temperature in the system $TlO_{1.5}$–BaO assuming Tl_2O_3 losses. The initial composition is $(TlO_{1.5})_{0.8}(BaO)_{0.2}$ in the two-phase field Tl_2O_3–Tl_2BaO_4. After a run up to 1200°C, the sample contains $Tl_2Ba_2O_5$, $Tl_2Ba_4O_7$ and $BaO_{1.3}$ in a non-equilibrium state. The $TlO_{1.5}$–BaO phase diagram is superimposed

decomposition to a crossing of a limit in the phase diagram. Figure 7 illustrates this behaviour for $(TlO_{1.5})_{0.75}(BaO)_{0.25}$ heated at 800°C. We can see a step in the Ln[–dLn(1–*r*)/d*t*]–Ln(*t*) plot corresponding approximately to Tl_2BaO_4 and $Tl_6Ba_4O_7$ if Tl_2O_3 vapour is supposed to be formed.

In the same system, $Tl_2Ba_2O_5$ with a congruent melting temperature of 1100°C may be used as a precursor for $Tl_2Ba_2CuO_6$, the first member of the $Tl_2Ba_2Ca_{n-1}Cu_nO_z$ series. Addition of CuO constraints the composition to change in a quasi-binary system. This procedure, carried out at high oxygen pressure (100 bars), permitted the formation of very pure samples and allowed us to understand the structural modifications in the compound [15, 27].

High activity is at present developed in $(Tl,Pb,Bi)(Sr,Ba)_2Ca_2Cu_3O_z$ which is one of the most promising material for future applications. Unfortunately the phase is formed competitively with (Tl,Pb)-1212 which acts as diffusion barrier. From DTA/TG it was demonstrated that heating up to 900°C significantly improves the crossing of this barrier but at this temperature in 1 bar of oxygen, the (Tl,Pb,Bi)-1223 phase decomposes so that a compromise has to be found. A first solution is to encapsulate the samples in sealed quartz tubes in which the equilibrium partial pressure of TlO_x at a given temperature fixes the composition. At 960°C, 12 h are sufficient to prepare high quality samples [28] but the method is difficult to transfer to high scale production. A second solution consisting to decrease the temperature of reaction at a level where diffusion is still efficient, is time consuming with commercially available powders. For example, at 880°C in oxygen flowing 120 h of anneal sketched by several grindings and Tl_2O_3 additions are needed to reproduce the quality of samples prepared in closed system. An interesting development is the production by spray pyrolysis of submicronic powders which, sintered for short period of time, produce nearly single phase. Actually, the difficulty in the system not

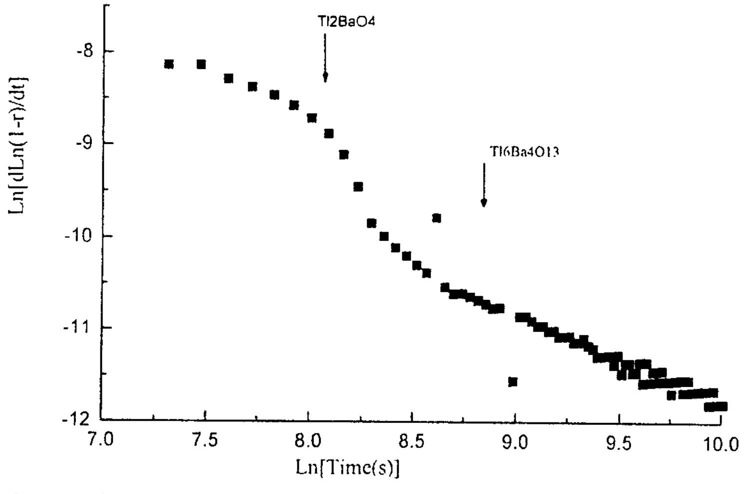

Fig. 7 Isothermal (800°C) analysis of $(TlO_{1.5})_{0.75}(BaO)_{0.25}$ in oxygen flowing. The rate of decomposition is expressed as the derivative of the Ln(1-*r*) with the time. If Tl_2O_3 is assumed to volatilize, the step in the range Ln(*t*)=7.9–8.7 corresponds to Tl_2BaO_4 and $Tl_6Ba_4O_{13}$

only concerns solid state equilibrium but also is to precise the high temperature phase diagram in order to determine the possibility for (Tl,Pb,Bi)-1223 to coexist with a liquid phase. The liquidus has been established for Tl/Pb = 1, when varying the Sr/Ba ratio [28] and was found to decrease from 1025°C for the Ba-free sample to 950°C for $(Tl_{0.5}Pb_{0.5})Ba_2Ca_2Cu_3O_z$, but the nature of phase(s) into equilibrium with the liquid is still uncertain. The condition of an existing (Tl,Pb)-1223 + liquid is of major importance for the preparation of textured samples.

In the (Pb,Bi)-2223 system, Majewski *et al.* [29] found such binary equilibrium in a restricted temperature-composition range. This information was successfully exploited by Noudem to produce large degree of texturation in ceramic samples [30]. In the same system, a significant progress is due to Jeremie [31] who investigated in detail the temperature of formation of Bi-2223, and studied the impurity effects both in phase equilibria and superconducting properties. The presence of a liquid phase was found to be determinant for the preparation of textured tapes of the compound with critical current as high as 40000 A cm^{-2} at 77 K [32].

Kinetic of oxygen uptake in cuprate superconductors

Thermogravimetric methods have been extensively used to determine the relations between the oxygen content, the critical temperature and structural modification in $YBa_2Cu_3O_{7-\delta}$ and to study the kinetics for reduction or oxidation. From the reversible oxygen removal at temperatures depending on the surrounding atmosphere, Monod *et al.* [33] were able to determine the phase diagram T_c-oxygen content. Haller *et al.* [34] showed that oxygen uptake in $YBa_2Cu_3O_{6+x}$ is an activated process with an activation energy of 111±3 kJ mol^{-1}. In samples highly textured, Fan *et al.* [35] separated the mechanism for oxygen absorption into chemical reaction and diffusion with activation energies in oxygen atmosphere of 105.2 kJ mol^{-1} and 68.4 kJ mol^{-1} respectively. We note that in this system, the step from $YBa_2Cu_3O_6$ to $YBa_2Cu_3O_7$, the extreme compositions for the Y-123 compounds, implies 2.40% of weight change.

In case of Bi-, Hg- and Tl-based systems, a modification of a few tenths of oxygen atoms in the molar formulae may lead to drastic modification of the superconducting properties. The weight losses (gain) are thus restricted to less than a percent and thermogravimetric measurements necessitate reliable equipment. With a symmetrical two-furnaces system we had access to the kinetic of the phase transition in $Tl_2Ba_2CuO_{6\pm\delta}$. At constant thallium content this compound can be prepared, as already mentioned, either in oxygen with an orthorhombic type structure or, in high argon pressure [15] with a tetragonal cell. The structural transformation from the latter to the former by annealing in oxygen is due to oxygen capture up to 0.15 atoms per formulae unit implying a weight increase of 0.30% [27]. The process was found to be thermally activated with E=78 kJ mol^{-1}. Due to thallium release at temperatures as low as 480°C in low oxygen partial pressure, the reversible transformation from orthorhombic to tetragonal is not possible but a transition from high- to low-oxidized orthorhombic phase was observed with the departure of 0.08 atom of oxygen per formulae unit with an activated energy E=150 kJ mol^{-1}. This value suggests that different cristallographic site than that involved in the tetragonal to orthorhombic transition are concerned. The existence of two orthorhombic phases involving interstitial oxygen sites in the system was recently detected by Attfield *et al.* [36] by resonant synchrotron X-ray powder diffraction in samples prepared in sealed tubes. The phase separation ortho(1)-ortho(2) is thought to be due to different occupation rates of interstitial oxygen but is claimed to concern 0.4 atoms, a value not consistent with 0.08 obtained by thermogravimetry on samples prepared under 100 bars of oxygen and expected to have a maximum state of oxidation.

Generalized oxidation studies

The metallic route

From the preceding sections it transpires that the problems related to the volatility of elemental oxides in HTSC may find solutions with use of high pressure techniques. This is a restrictive view for applications and early in the search for preparing HTSC, the oxidation of metallic precursors was proposed. Usually a metallic ribbon obtained by the quench of a liquid alloy is oxidized. The method was applied by Luo *et al.* [37] to Bi- and Y-series. The critical current was substantially increased in $EuBa_2Cu_3O_{7-x}$ and provided homogeneous $(Bi_{0.7}Pb_{0.3})_2Sr_2Ca_2Cu_3O_x$. Gao *et al.* [38] incorporated Ag in a Bi(Pb)-Sr-Ca-Cu precursor leading to a significant improvement of the mechanical properties of the corresponding superconducting phase and to an increase of the critical current.

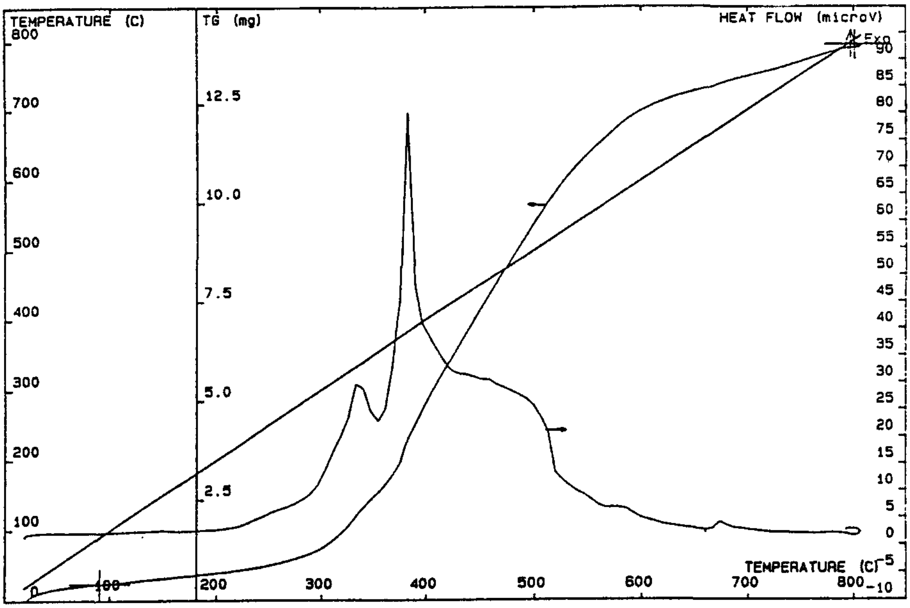

Fig. 8 DTA and TG curves of $TlBa_2Ca_3Cu_4$ in oxygen. Heating rate: 10°C min^{-1}. Oxidation starts at 300°C and a violent exothermic reaction due to the formation of a mixed oxides occurs in the range of 400–500°C. At 800°C total oxidation is not realized but the sample contained 18% of superconducting phase with $T_c = 110$ K

In fact, the procedure is more suitable for systems containing a volatile component for which the oxidation treatment can be performed at moderate temperatures. For thallium compounds an interesting proportion of superconducting phases could be prepared by oxidizing alloys in the Tl–Ba–Ca–Cu system at 700°C [39]. An example is given in Fig. 8 showing the DTA/TG of $TlBa_2Ca_3Cu_4$ heated at a rate of 10°C min^{-1}. The exothermic reaction of formation of single or mixed oxides is observed at temperatures as low as 300°C comesponding to a weight increase of 17%. As evidence, the superconducting phase expected from the initial composition of the alloy is not completely formed during the DTA/TG run but the experiment indicates a continuous evolution of the oxidation at 600°C. When annealed for 48 h at 700°C a mixture of $TlBa_2CaCu_2O_x$ and $Tl_2Ba_2Ca_2Cu_3O_y$ with critical temperatures $T_c=90$ K and $T_c=120$ K respectively is formed [40]. The proportion of superconducting phases is approximately 30% but could be increased up to 45% in compounds with different compositions opening thus a new route for the preparation of HTSC.

Conclusion

A brief review of the use DTA/TG for the study of high temperature superconductors has been presented. The main interest of this assembly, coupling heat and weight changes measurement, is for the determination of phase relations with, as immediate consequence, implications in elaboration processes. Over stepping this field of phase equilibrium analysis, DTA/TG may be a powerful tool for the test of the purity of the components, eventually revealing new intermediate oxide compounds. The oxidation of complex metallic system in order to form the corresponding superconducting phase may be investigated and, with help of X-ray diffraction analysis, the mechanisms for oxidation may be proposed. Taking advantage of increased accuracy of modern systems, a quantitative analysis of the reaction kinetics is now available from DTA/TG curves. The possibility to access to the activation energies for a given reaction, specially oxygen capture and release, may be an important step for the understanding of high temperature superconductivity.

* * *

It is a pleasure to associate to this lecture my colleagues from research groups with which I collaborate from many years in the difficult field of elaboration and characterization of thallium-based HTSC: T. K. Jondo, K. Lebbou. R. Abraham and M. T. Cohen-Adad in Lyon (Lab. PCM2), M. Couach and A. F. Khoder at the CEN in Grenoble (SPSMS), J. Muller and R. Flukiger at the DPMC in Geneva and of course C. Opagiste and Ph. Galez at the LSM in Annecy.

References

1 A. Prince "Historical Development of Alloy Phase Diagram Studies in the 19th and Early 20th Centuries", JCAT 91, 22èmes Journées de Calorimétrie et d'Analyse Thermique, 27–29 Mai 1991, Chatenay-Malabry.
2 F. Rudberg and K. Svenska, Vet. Akad. Hand. (1929).
3 W. C. Roberts-Austen, Metallographist, 2 (1899) 186.
4 K. Honda, Sci. rep. Tohoku Univ., 1 (1915) 97.

5 J. Muller, Reports on Progress in Physics, 43 (1980) 641.
6 R. Flukiger, Chapter 8 of Superconductor Materials Science, Eds. S. Foner, B. B. Schwartz, Plenum Publ. Corp., 1981.
7 J. L. Jorda, Thesis University of Geneva, 1980, p. 1934.
8 J. L. Jorda, R. Flukiger and J. Muller, J. Mater. Sci., 13 (1978) 2471.
9 D. C. Johnston, R. N. Shelton and J. J. Buga, Solid State Comm., 21 (1977) 949.
10 R. Flukiger, R. Baillif, J. Muller and K. Yvon, J. Less Common Metals, 21 (1980) 193.
11 R. E. Gladyshevskii, Ph. Galez, K. Lebbou, J. Allemand, R. Abraham, M. Couach, R. Flukiger, J. L. Jorda and M. Th. Cohen-Adad, Physica C, 267 (1996) 93.
12 L. S. Palatnik and A. I. Landau, "Phase equilibria in multicomponent systems", Holt, Rinehart & Winston, New York 1964.
13 A. Sebaoun, Xièmes JEEP, Tours, 23. Mars 1984, Ed. R. Ceolin.
14 F. N. Rhines, "Phase diagrams in metallurgy", McGraw-Hill 1956.
15 C. Opagiste, G. Triscone, M. Couach, T. K. Jondo, J. L. Jorda, A. Junod, A. F. Khoder and J. Muller, Physica C, 213 (1993) 17.
16 T. Graf, Thesis Univ. Geneva, 1991, p. 2480, .
17 Y. L. Chen and R. Stevens, J. Amer. Ceram. Soc., 75 (1992) 1160.
18 G. Triscone, J. Y. Genoud, T. Graf, A. Genoud and J. Muller, Physica C, 176 (1991) 247.
19 F. Parmigiani, G. Chiarello, N. Ripamonti, H. Goretzki and U. Roll, Phys. Rev. B, 36 (1987) 7148.
20 T. Itoh, A. Yasuda, S. Nonomura and S. Nitta, Physica C, 185–189 (1991) 595.
21 M. Huvé, C. Michel, A. Maignan, M. Hervieu, C. Martin and B. Raveau, Physica C, 205 (1993) 219.
22 A. F. Mayorova, S. N. Mudretsova, M. M. Mamontov, P. A. Levashov and A. D. Rusin, Thermochim. Acta, 217 (1993) 241.
23 T. K. Jondo, Thesis Univ. Lyon, Mars 1994.
24 R. Schmid, Metallurgical Trans. B, 14B (1983) 473.
25 J. L. Jorda and M. T. Saugier Cohen-Adad, J. Less Common Metals, 171 (1991).
26 W. L. Holstein, J. Phys. Chem., 97 (1993) 4224.
27 J. L. Jorda, T. K. Jondo, R. Abraham, M. T. Cohen-Adad, C. Opagiste, M. Couach, A. F. Khoder and G. Triscone, J. Alloys and Compounds, 215 (1994) 135.
28 K. Lebbou, R. Abraham, S. Trosset, M. Th. Cohen-Adad, J. L Jorda and Ph. Galez, XXIèmes J.E.E.P, 24–25 April 1995, Rouen.
29 P. Majewski, B. Hettig, K. Schulze and G. Petzow, Adv. Materials, 3 (1991) 488.
30 J. G. Noudem, J. Beille, D. Bourgault, A. Sulpice and R. Tournier, Physica C, 235–240 (1994) 3401.
31 A. Jeremie, Thesis Univ. Geneva, 1995, p. 2762.
32 R. Flukiger, B. Hensel, A. Jeremie, M. Decroux, H. Kupfer, W. Jahn, E. Seibt, W. Goldacker, Y. Yamada and J. Q. Xu, Supercond. Sci. & Technol., 5 (1992) S61.
33 P. Monod, M. Ribault, F. d'Yvoire, J. Jegoudez, G. Collin and A. Revcolevschi, J. Physique, 48 (1987) 1369.
34 I. Haller, M. W. Shafer, R. Figat and D. B. Goland, in "Chemistry of Oxide Superconductors", C.N.R. Rao Ed. Blackwell, London 1988, p. 93.
35 Z. G. Fan, Y. X. Zhuang, G. Yang, R. Shao and G. F. Zhang, J. Alloys and Compounds, 200 (1993) 33.
36 J. P. Attfield, M. A. G. Aranda and D. C. Sinclair, Physica C, 235–240 (1994).
37 J. S. Luo, J. P. Chevalier and D. Michel, Material Sci. & Engineer., B3 (1989) 325.
38 W. Gao, S. C. Li, D. A. Rudman and J. B. Vander Sande, Physica C, 167 (1990) 395.
39 J. L. Jorda, R. Abraham, M. T. Cohen-Adad, M. Couach and A. F. Khoder, Materials Letters, 11 (1991) 326.
40 M. Couach, A. F. Khoder, F. Monnier, J. L. Jorda, M. T. Cohen-Adad and R. Abraham, "Irreversibility and Reversibility of high T_c thallium based compounds studied by AC susceptibility" in High Temperature Superconductors, P. Vincenzini Ed. 1991 p. 353.