Journal of Thermal Analysis, Vol. 40 (1993) 373-378

THERMAL PROPERTIES OF HIGH-T_c SUPERCONDUCTORS

G. E. Nikiforova, V. B. Lazarev and I. S. Shaplygin

KURNAKOV INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY, RUSSIAN ACADEMY OF SCIENCES, LENINSKY PR., 31, MOSCOW, 117907 RUSSIA

The termal stabilities of several families of high-T_c superconductors (HTSC), as well as the dependence of phase transitions on temperature and stoichiometry, have been studied by X-ray diffraction, DTA, TG and DSC. Experimental results are discussed in the context of decomposition models.

Keywords: DSC, DTA, high-T_c superconductors, phase transitions, TG, X-ray

Introduction

During the last five years at least four families of mixed oxide ceramic materials have been shown to be superconducting: (1) $La_{1-x}Ca(Sr,Ba)_xCuSO_4$, (2)$YBa_2Cu_3O_{7-x}$ and other compounds 1–2–3, (3) complex oxides of Bi–Sr–Ca–Cu and (4) complex oxides of Tl. Among the most promising of these high-T_c superconductors are ceramic compositions in the systems Ln–Ba–Cu–O (where *Ln* represents Y and rare earth elements), Bi–Sr–Ca–Cu–O and Tl–Ba–Ca–Cu–O. Critical transition temperatures for these compounds are above 78 K. One of the characteristics of the mixed oxides of interest is their thermal properties. From numerous experimental data it has been shown that many HTSC are thermodynamically unstable [1, 2]. Therefore it is important to investigate their thermal stabilities and other properties at elevated temperatures.

Results and discussion

Earlier thermal behaviour of ceramic HTSC in the systems $La_{2-x}M_xCuO_{4-\delta}$ (M = Ca, Sr, Ba) and $LnBa_2Cu_3O_{7-y}$ (as typical members of 1–2–3 compounds) has been studied by DTA under dynamic conditions; the stochiometric depen-

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

dence of electrical properties of the high-T_c superconductors has been also investigated [3–11].

The thermal properties of the model substance La_2CuO_4 (which under certain conditions is also a HTSC with a transition temperature of 26–38 K [15] have been studied with the aim of understanding the thermal decomposition process for complex oxides. This oxide decomposes at heating above 1150°C according to the reaction:

$$2La_2CuO_4 \xrightarrow{-y\,O_2} 2La_2CuO_{4-y/2} \longrightarrow 2La_2O_3 + Cu_2O + (0.5-y)\,O_2 \qquad (1)$$

Equation (1) is also common to the thermal decomposition of other isostructural (or pseudoisostructural) members of the series Ln_2CuO_4 or high-T_c oxide superconductors $Nd_{2-x}(Ce,Th)_xCuO_{4-y}$.

The decomposition temperature and solid residue after decomposition of the mixed oxide allows distinction of members of this series [9, 12–15].

The abundance of experimental data on thermal stabilities of different oxide superconductors in the above systems presents the opportunity to obtain data on thermal properties and the influence of temperature on superconducting properties for high-T_c superconductors with differing cation compositions and oxygen deficiencies [16].

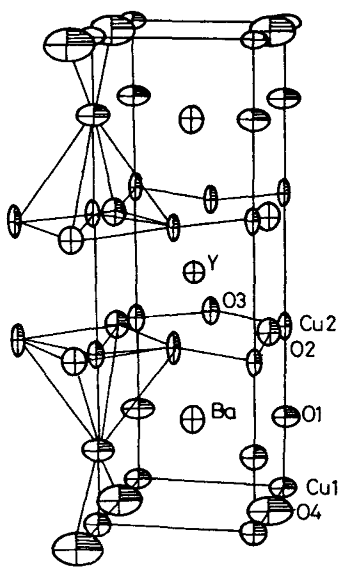

Fig. 1 Crystalline structure of $YBa_2Cu_3O_7$

Thermal stabilities of 1–2–3 type compounds will be demonstrated using $YBa_2Cu_3O_{6+x}$ as an example. This is a compound with a T_c near 90 K and a transition width of less than 2 K. Amounts of oxygen in these compounds have been determined by a volumetric method [16] and a parallel iodine titrimetric method. Starting from the ideal formula $YBa_2Cu_3O_7$ (Fig. 1) and unit-cell parameters of the orthorhombic lattice $a = 3.8206$ Å, $b = 3.8553$ Å, $c = 11.675$ Å, it was possible to calculate the mechanism of oxygen evolution from the matrix and determine the mass loss on TG curves.

For correct interpretation of thermal decomposition processes of such samples it is necessary to minimize the influence of the atmosphere in contact with the sample. The thermal decomposition process of the sample is strongly influenced by the ambient partial oxygen pressure, although the solid residue has practically the same composition.

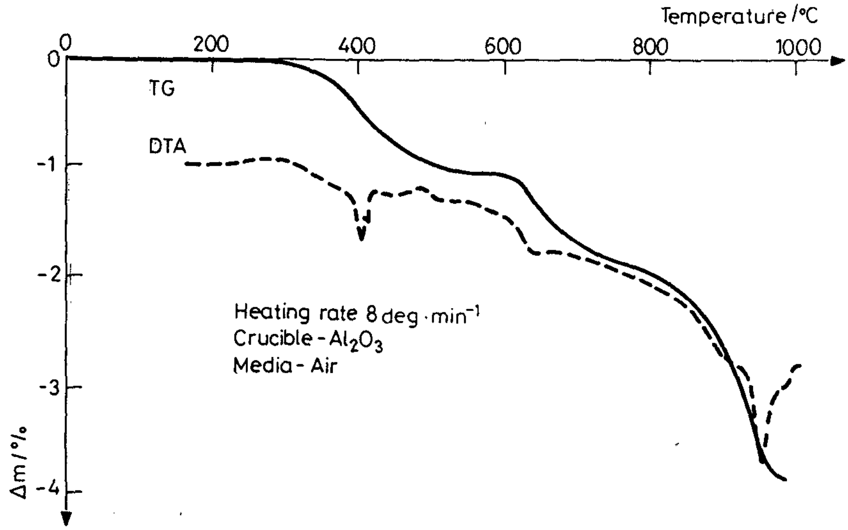

Fig. 2 DTA–TG curves for $YBa_2Cu_3O_7$ in air at a heating rate 8 deg·min^{-1}

Pyrolysis in a platinum crucible may be complicated to interpret because of the catalytic effect of the platinum; particular effects of gas media and other experimental conditions on decomposition mechanisms are given in [17–27].

It is apparent from Fig. 2 that thermal decomposition of $YBa_2Cu_3O_7$ involves several oxygen loss stages:

(i) between 330°C–360°C oxygen evolution from O(4) sites occurs and from XRD data this would appear to coincide with early transformation from orthorhombic to tetragonal structure;

(ii) from 400°–440°C to about 750°C a slow oxygen dissociation from O(3) and O(2) sites is observed with practically equal values of dissociation energy from both sites;

(iii) above 850°C evolution of part of the oxygen from O(1) sites occurs, followed by dissociation of the high-T_c oxide into several non-superconducting oxides or metallic copper. Thermal decomposition of high-quality single crystals of the 1–2–3 type can differ in detail from the scheme shown in Fig. 3 because of anionic defect ordering.

The dynamics of decomposition of these compounds may be represented by the following scheme (see also Fig. 3). Thermal decomposition begins in air (average partial oxygen pressure 0.21 bar) at 330°–360°C.

Later, gradual oxygen evolution from O(3) and O(2) occurs, until complete disappearance of the tetragonal structure. Earlier workers have suggested that this decomposition may be associated with appearance of a tetragonal sublattice of type Y–(Y–Ba–Cu)–Y–Cu. The final solid products of the decomposition are the phases $Y_2Cu_2O_5$, Y_2BaCuO_5, $Ba_2Y_2O_5$, Cu_2O, the exact amounts depending on the heating rate and final temperature.

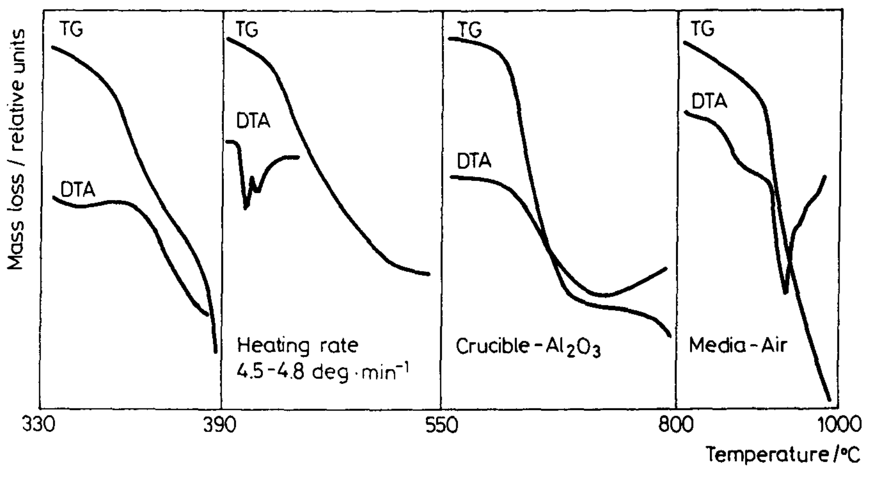

Fig. 3 DTA–TG curves for 1–2–3 superconductor systems at different decomposition stages

For compounds in the system, Bi–Sr–Ca–Cu–O and Tl–Ba–Ca–Cu–O, thermal decomposition is affected by different factors, in particular evaporation of certain components such as thallium oxides on heating in air, and interactions with container material.

For high-T_c phases in the system Bi–Sr–Ca–Cu–O a number of thermal effects depend on sample stoichiometry, stabilizing additions (PbO, Sb_2O_3), preparation, and heat treatment conditions.

In summary, definition of a thermal decomposition mechanism for superconducting high-T_c phases 2212, 2223 and 2334 in the system Tl–Ba–Ca–Cu–O (independent of conditions of synthesis and real thermal decomposition mechanisms), requires that the extent of thallium removal from the sample has first to be determined. This procedure needs close control of experimental procedure and exact definition of intermediates at each stage.

References

1 P. L. Gai and J. M. Thomas, Supercond. Review, 1 (1992) 1.
2 A. W. Sleight, Physics Today, 44 (1991) 24
3 I. S. Shaplygin, I. A. Konovalova, V. B. Lazarev and E. A. Tistchenko, Letters to JETPh, 46 (1987) Application, p. 152.
4 E. A. Tistchenko, I. S. Shaplygin, I. A. Konovalova and V. B. Lazarev, Inorganic Materials (Russ., translated to English), 23 (1987) 2105.
5 N. K. Belsky, L. I. Ochertyanova, I. A. Konovalova and I. S. Shaplygin, Inorganic Materials (Russ., translated to English), 24 (1983) 976.
6 I. S. Shaplygin, I. A. Konovalova, E. A. Tistchenko and V. B. Lazarev, J. Inorganic Chemistry (Russ., translated to English), 33 (1988) 1928.
7 I. S. Shaplygin, V. B. Lazarev, E. A. Tistchenko and I. A. Konovalova, J. Inorganic Chemistry (Russ., translated to English), 33 (1988) 2153.
8 V. B. Lazarev, I. S. Shaplygin, I. A. Konovalova and K. S. Gavrichev, Physica C, 153–155 (1988) 1024.
9 I. A. Konovalova, V. B. Lazarev, E. A. Tistchenko and I. S. Shaplygin, J. Thermal Anal., 33 (1988) 883.
10 V. B. Lazarev, K. S. Gavrichev, V. E. Gorbunov, J. H. Greenberg and I. S. Shaplygin, Thermochim. Acta, 174 (1991) 27.
11 G. A. Sharpataya, Z. P. Ozerova, I. A. Konovalova, V. B. Lazarev and I. S. Shaplygin, Inorganic Materials (Russ., translated to English), 27 (1991) 1674.
12 I. S. Shaplygin, A. A. Zakharov, I. A. Konovalova and V. B. Lazarev, Hungarian Symp. of Thermal Analysis, Workbook, Hungary, Budapest, June 10–12, 1981, p. 72.
13 V. B. Lazarev and I. S. Shaplygin, J. Inorganic Chemistry (Russ., translated to English), 26 (1981) 1755.
14 I. A. Konovalova, I. S. Shaplygin and V. B. Lazarev, J. Inorganic Chemistry (Russ., translated to English), 34 (1989) 522.
15 A. I. Popov, I. A. Konovalova, E. A. Tistchenko and I. S. Shaplygin, Inorganic Materials (Russ., translated to English), 25 (1989) 345.
16 E. Kaisersberger, M. Gebhardt, E. Post and I. Opfermann, 5th European Symp. on Thermal Analysis, 25–30 Aug. 1991, France, Nice.
17 T. B. Lindemer, F. A. Washburn, C. S. McDougall, R. Feenstra and O. Cavin, Physica C, 178 (1991) 93.
18 P. Schleger, W. N. Hardy and B. X. Yang, Physica C, 176 (1991) 261.
19 F. H. Gazzon, I. D. Raistrick, D. S. Gingley and J. W. Halloran, J. Mater. Res., 6 (1991) 885.
20 G. Geder, R. McCormack and D. de Fontaine, Phys. Rev. B, 44 (1991) 2377.
21 I. S. Shaplygin and V. B. Lazarev, Mat. Res. Bull., 10 (1975) 903.
22 I. S. Shaplygin and V. B. Lazarev, Thermochim. Acta, 20 (1977) 381.

23 I. S. Shaplygin and V. B. Lazarev, Thermochim. Acta,32 (1979) 53.
24 I. S. Shaplygin and V. B. Lazarev, Thermochim. Acta,33 (1979) 225.
25 I. S. Shaplygin and V. B. Lazarev, Thermochim. Acta,41 (1980) 320.
26 I. S. Shaplygin and V. B. Lazarev, J. Inorganic Chemistry, (Russ., translated to English), 26 (1981) 46.
27 I. S. Shaplygin and V. B. Lazarev, J. Inorganic Chemistry, (Russ., translated to English), 31 (1986) 3181.

Zusammenfassung — Mittels Röntgendiffraktion, DTA, TG und DSC wurde sowohl die thermische Stabilität verschiedener Arten von Hoch-T_c Supraleitern (HTSC) als auch die Abhängigkeit der Phasenumwandlungen von Temperatur und Stöchiometrie untersucht. Die experimentellen Ergebnisse wurden im Zusammenhang mit Zersetzungsmodellen diskutiert.