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THERMAL ANALYSIS IN THE STUDY OF THE NEW OXIDE-BASED SUPERCONDUCTORS

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Thermoanalytical methods offer a convenient means for testing the starting materials used in the synthesis of the ceramic superconductors and for establishing the reaction and annealing temperatures as well as the stoichiometry of the end product. In addition, the stability and other thermal properties of the superconducting materials can be investigated including phase transformations during thermal cycling and possible reactions with substrates and the environment. The applications of TG, DSC/DTA and other thermal techniques for the study of the $YBa_2Cu_3O_{7-x}$ superconductor are briefly reviewed using results from own experiments and selected literature data to illustrate the examples given.

Probably the most numerous applications of thermal analysis are within materials science. Especially useful the thermoanalytical methods have proven to be in the study of the newly discovered oxide-based high-temperature superconductors. The present paper will discuss how thermal methods of analysis can be used to aid the preparation and characterization of the ceramic superconductors, most notably the $YBa_2Cu_3O_{7-x}$ and related phases.

Although most TA experiments deal with the so-called 1-2-3 compound or the $LnBa_2Cu_3O_{7-x}$ phase, where Ln is Y or other rare earth, it is obvious that thermoanalytical methods can be used to study the bismuth and thallium containing compounds and other high-T_c phases, too. Structurally and thermodynamically all these families of high-T_c superconductors have much in common. A typical structural feature, for instance, is the presence of planes consisting of copper atoms surrounded by four strongly bonded oxygens. In $YBa_2Cu_3O_{7-x}$ these CuO planes (Cu2) are separated by an yttrium layer and intercalated by two barium-oxygen layers and by one crystallographically distinct copper-oxygen layer where the Cu1 atoms form one-dimensional chains with oxygen (Fig. 1). The superconductor families based on thallium and bismuth have more complicated stoichiometries due to multi-layered structures [2, 3].

As the thermoanalytical literature of these new materials is already very extensive, rapidly expanding and furthermore partly available only as preprints or conference proceedings, the literature references of this review will be selective and not aiming at completeness. Most points will be discussed through examples based on authors' own experimental data or on few representative reports from the literature.

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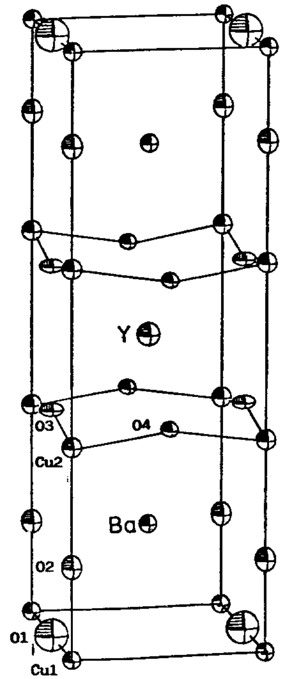

Fig. 1 Crystal structure of $YBa_2Cu_3O_{7-x}$ as determined by neutron diffraction [1]

Thermal studies

The various areas, where thermoanalytical methods can be applied, may be grouped as follows:

- Preparation
- Stoichiometry
- Thermal expansion and related properties
- Phase transformations
- Chemical reactions

While TG and DTA/DSC (and their simultaneous combinations) have been used in most studies, the obtaining of certain data requires other techniques such as EGA, dilatometry etc. In any case, standard commercial TA apparatus available in many laboratories and reaching moderately high temperatures (up to 1200°C) is sufficient for these studies.

Preparation

The new oxide-based superconductors are synthetized in bulk form using high-temperature thermal synthesis involving the mixing or precipitating the starting materials into a homogeneous mixture and then heating and annealing the mixture under strict atmospheric and temperature control. These steps may be repeated and, in order to ensure better contact between the reacting particles, compressing into pellets is usually applied.

In the case of $YBa_2Cu_3O_{7-x}$, various starting materials (oxides, carbonates, nitrates, oxalates, organic complexes etc.) have been used. All except sulfur containing species ($BaSO_4$ formation) seem to work well although the presence of carbon in the final product may be disadvantageous for aplications. TG is a very convenient method for a preliminary check of the decomposition mechanism and temperatures of the individual starting materials. During the thermal synthesis it can be used to monitor the temperature and completeness of the formation reaction, see Fig. 2 and refs. [4–6], for instance.

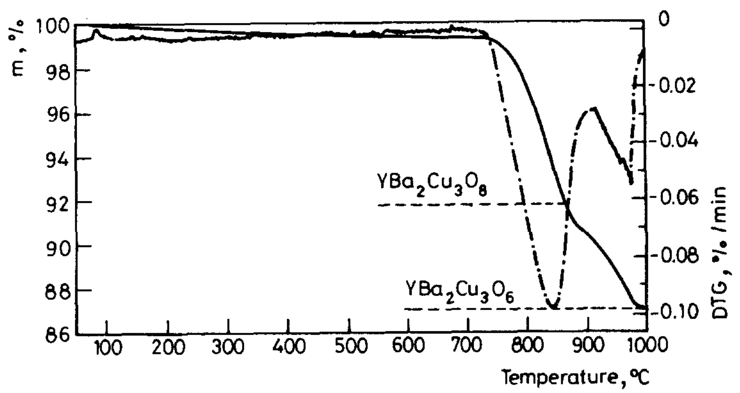

Fig. 2 The formation of $YBa_2Cu_3O_n$ phases upon heating in air of a starting mixture consisting of Y_2O_3, $BaCO_3$, CuO in molar ratio 1:4:6

Stoichiometry

The crucial requirements for superconductivity and high critical temperature of the $YBa_2Cu_3O_{7-x}$ phase are that the crystal structure is orthorhombic and the yttrium/oxygen ratio is close to 7 which means that x is small or around 0.1.

The extra oxygen (01 atoms in Fig. 1) is easily removed when temperature exceeds 500°C and a semiconducting, tetragonal $YBa_2Cu_3O_6$ phase is formed. Fortunately, slow cooling and annealing under sufficient oxygen pressure (air, for instance) leads to the recovery of the oxygen stoichiometry required for superconductivity. This can be monitored by TG (Fig. 3).

The formal oxidation state of copper in the superconducting $YBa_2Cu_3O_{7-x}$ exceeds two and can be determined besides by the conventional chemical method (iodometric titration) also by reduction in hydrogen [7]. This is most conveniently carried out in a thermal balance allowing an easy following and control of the reaction.

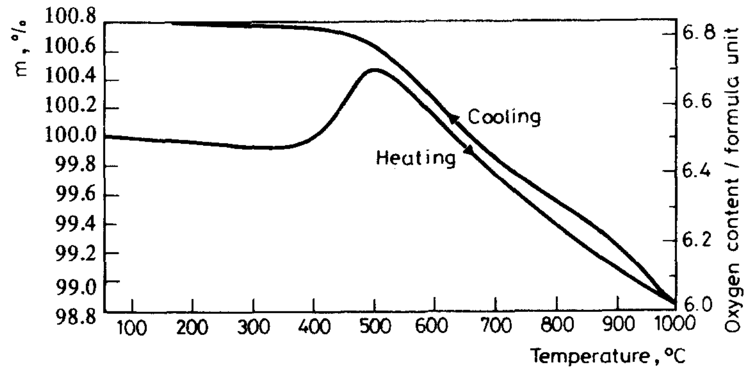

Fig. 3 TG data for $YBa_2Cu_3O_{6.5}$ in air showing the effect of heating and cooling on the oxygen content of the sample

The overall reaction is

$$2\,YBa_2Cu_3O_{7-x} + (7-2x)\,H_2 \rightarrow Y_2O_3 + 4\,BaO + 6\,Cu + (7-2x)\,H_2O$$

but from the TG curve presented in Fig. 4 is obvious that the reduction proceeds via several intermediate steps which do not, however, seem to correspond to distinct phases.

A comparison between the various chemical methods to determine the oxygen stoichiometry and the copper oxidation state shows a good internal agreement [8].

Thermal expansion

From the point of view of applications, thermal expansion is an important factor, especially for thin films grown on a substrate. Coefficient of thermal expansion α has been determined for $YBa_2Cu_3O_{7-x}$ by several

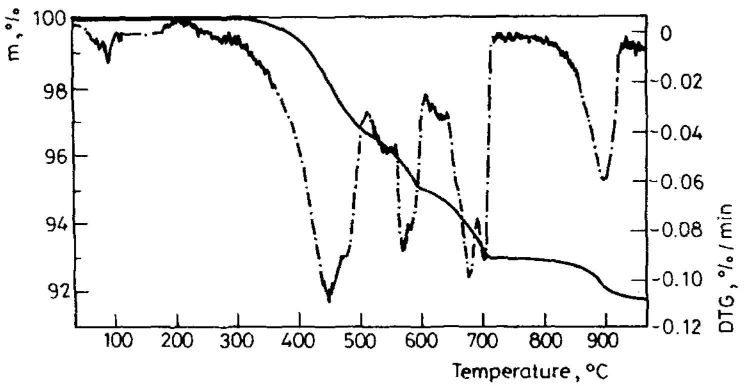

Fig. 4 TG and DTG (broken line) curves of $YBa_2Cu_3O_{7-x}$ in reducing atmosphere (5% H_2, 95% Ar)

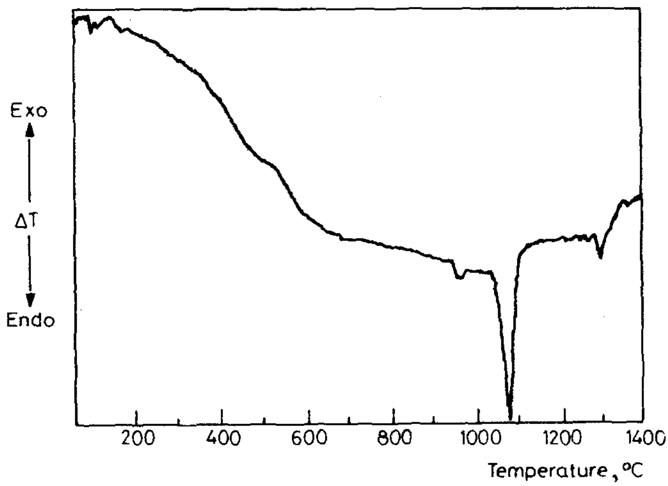

Fig. 5 DTA curve of $YBa_2Cu_3O_{7-x}$

groups and there appears to be several temperature regions with different slopes of thermal expansion. The α values show a reasonably good agreement when measured by different groups and techniques, however [9–11].

Phase transformations

At a first sight, the DTA/DSC curve of $YBa_2Cu_3O_{7-x}$ up to 1100° is not very complicated but shows only one major peak located slightly around 1000° (Fig. 5). This endotherm can be attributed to the melting of the sample and its position is somewhat dependent on the atmosphere [12]. There are also usually a few smaller endotherms in the range 800–960° but their origin is not unequivocal (Table 1.) Furthermore, the thermal history of the sample affects the DTA curve and repeated thermal cycling produces new, endothermic peaks below 1000° [13, 14].

Table 1 Small endotherms in the range 800–960°C as observed in the DTA curves.

Temperature °C	Reference
818, 899, 957	14
893, 899, 940	15
920–960	16
940	17

The tetragonal-orthorhombic transformation around 600° involves, as discussed above, a change in the oxygen stoichiometry. Consequently it can be seen in the TG curve as well as in EGA curves [10]. It is also more or less clearly visible in the DTA/DSC curves.

The best way to follow this transformation is to use high-temperature X-ray diffraction, however [18, 19]. In spite of the similarities of the diffraction patterns there are maxima around $2\theta = 33°$ where the intensity ratio of the two peaks is different in the tetragonal and orthorhombic phases allowing an easy identification (Fig. 6.).

Chemical reactions

Apart from the absorption and desorption of oxygen and other gases, the $YBa_2Cu_3O_{7-x}$ phase being thermodynamically unstable reacts with water vapor and carbon dioxide forming readily Y_2BaCuO_5, $BaCO_3$ and other phases. It also possesses considerable catalytic activity [20].

For most applications in microelectronics, the superconductors have to be prepared in the form of thin films. The possible reactions with substrate materials and various other layers in contact with the superconducting layer can be studied by DTA/DSC although only a few studies appear to have been done so far [21].

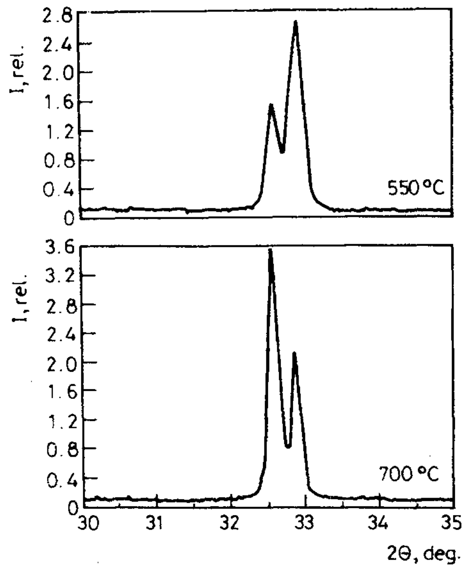

Fig. 6 High-temperature X-ray diffraction diagrams of the orthorhombic (550°C, upper curve) and the tetragonal (700°C, lower curve) $YBa_2Cu_3O_{7-x}$-phases

Concluding remark

The discovery of the new high-T_c superconductors has greatly stimulated research in chemistry, physics and engineering. Thermoanalytical methods have proven to be almost indispensable in solving some of the problems related to the preparation and stoichiometry of phases, for instance. Furthermore, the application of thermal analysis is in most cases convenient and straightforward and can be done with the existing standard apparatus.

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Zusammenfassung – Thermoanalytische Methoden eignen sich zum Erproben von Ausgangsmaterialien zur Synthese von Keramiksupraleitern und zur Ermittlung der Reaktions- und Glühtemperaturen sowie der stöchiometrischen Zusammensetzung der Endprodukte. Außerdem können die Stabilität und andere thermische Eigenschaften der supraleitenden Materialien, einschließlich deren Phasenübergängen beim Wärmecycling sowie möglicher Reaktionen mit Substraten oder mit der Umwelt untersucht werden. Es wird kurz die Anwendung von TG-, DSC/DTA- und anderen thermischen Verfahren bei der Untersuchung des Supraleiters $YBa_2Cu_3O_{7-x}$ beschrieben sowie Ergebnisse aus eigenen Experimenten un zur Illustration der aufgeführten Beispiele ausgewählte Literaturangaben gegeben.

Резюме - Термоаналитические методы предпочитают использовать обычно для проверки исходных материалов, используемых при получении сверхпроводящей керамики, для определения температур реакции и аннелирования, а также для установления стехиометрии конечного продукта. Однако, этими же методами могут быть изучены устойчивость и другие термические свойства сверхпроводящих материалов, включая фазовые превращения во время термического цикла и возможные реакции с подложкой и окружающей средой. В сжатой форме приведено обозрение по применению ТГ, ДСК/ДТА и других термических методов для изучения сверхпроводника $YBa_2Cu_3O_{7-x}$, используя собственные опыты, а также литературные данные.