

## THE DECOMPOSITION OF EDTA-GEL PRECURSORS IN THE PRODUCTION OF BSCCO SUPERCONDUCTORS

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The decomposition of EDTA gel precursors for BSCCO superconductor manufacture has been studied using STA (TG/DTA) and dilatometry in conjunction with FTIR. The thermoanalytical data are discussed in relation to the sequence of phase formation necessary for the production of the 2223 BSCCO superconducting phase. The effects of substitution of Pb for Bi on the temperatures of formation of the superconducting phases is also discussed. STA has also been carried out under varying oxygen partial pressures to determine the effects of oxygen pressure on the formation and decomposition of the phases involved in the production of the 2223 compound.

**Keywords:** superconductor, STA (TG/DTA) and dilatometry

### Introduction

In the Bi–Sr–Ca–Cu oxide system three superconducting phases exist, with perovskite structures and nominal composition  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$  ( $n = 1$  to 3)[1–3]. These phases, which have different numbers of  $\text{CuO}_2$  layers, are the 2201 phase ( $c = 24.6 \text{ \AA}$ ,  $n = 1$ ), the 2212 phase ( $c = 30.9 \text{ \AA}$ ,  $n = 2$ ) and the 2223 phase ( $c = 37 \text{ \AA}$ ,  $n = 3$ ), with  $T_c$ 's of 10 K, 90 K and 110 K respectively. Many attempts have been made to prepare the 2223 phase by various sol-gel methods [4–6] to overcome the problems associated with conventional ceramic processing. These problems have been identified to be contamination and deviation of stoichiometry because of chemical inhomogeneity and segregation.

In this paper the use of ethylene-diamine-tetra-acetic acid (EDTA) as the organic complexing agent for gel formation is described. To ensure that the homogeneous nature of the gel precursor is carried into the end-product, the decomposition/oxidation process has to be understood. Accordingly, a thermoanalytical study has been made of the decomposition of the gel precursor for the 2223 phase. Because of the similarities in crystal structures and free energies of formation of the three phases it is very difficult to prepare pure 2223 phase [7].

Hence the effects of Pb-doping of the gel and the use of different oxygen partial pressures during firing have also been studied.

## Experimental procedure

### *Precursor production*

High-purity metal nitrates were dissolved in deionised water.  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was dissolved with the aid of  $\text{HNO}_3$ . The molar ratio of EDTA: metal nitrates was kept at 1:1 to ensure the presence of enough acid for bonding with the metal ions. The *pH* of the solution was kept at 6 by the addition of  $\text{NH}_4\text{OH}$  solution. The solution was dehydrated to form the amorphous precursor using a rotary evaporator and a vacuum oven [4, 5].

### *Thermal analysis*

The precursor decomposition was studied using a SEIKO 320 simultaneous TG/DTA facility. 10 mg samples were heated at rates of 3 to 10  $\text{deg}\cdot\text{min}^{-1}$  in Pt crucibles under various oxygen partial pressures (100 ml/min flow rate). Subsequently, the precursor was calcined in two stages at 300° and 700°C. After ball milling the calcined powders were pressed into pellets (3.5 mm d., 4 mm h.) using pressures of 370  $\text{MN m}^{-2}$ . The sintering behaviours of the pellets were determined using dilatometry, with a sensitivity of  $\pm 5 \cdot 10^{-6}$  m, in flowing air. Heating rates of 3–10  $\text{deg}\cdot\text{min}^{-1}$  were used.

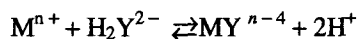
### *Material characterization*

The precursor and oxide products were characterized by XRD using  $\text{CuK}_\alpha$  radiation and a Philips diffractometer. Compositions of the phases in the sintered samples were determined by EDX analysis and scanning electron microscopy. Critical temperature onsets were determined in an Oxford Instruments Vibrating Sample Magnetometer (VSM). Fourier-transform infrared spectroscopy (FTIR) was used to characterise products obtained after heating to various critical temperatures indicated by thermal analysis.

## Results and discussion

### *Precursor formation and decomposition*

The formation of the organometallic precursors depends on *pH*. In neutral to moderately basic solutions EDTA combines with metal ions in a 1:1 ratio [8] as:



(where  $Y$  refers to EDTA)

Use of a  $pH$  of 6 ensures the formation of the complex without any precipitation. From the FTIR data in Fig. 1 it is clear that complex formation has taken place, as the presence of the  $1600\text{ cm}^{-1}$  absorption refers to antisymmetrical stretching of carboxylate groups  $-\text{COO}^-$  which are acid groups binding metal ions [9, 10].

Simultaneous TG/DTA for the decomposition of the precursor are given in Fig. 2 where three stages can be identified. The first stage is dehydration, this taking place between  $50^\circ\text{--}150^\circ\text{C}$ . The second stage, between  $150^\circ$  and  $400^\circ\text{C}$ , is the initial decomposition of the organic-nitrate complex, which gives rise to the evolution of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and nitrous oxide. The third stage is the final decomposition of the precursor between  $400^\circ\text{--}500^\circ\text{C}$  with the further removal of organic material as  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are evolved.

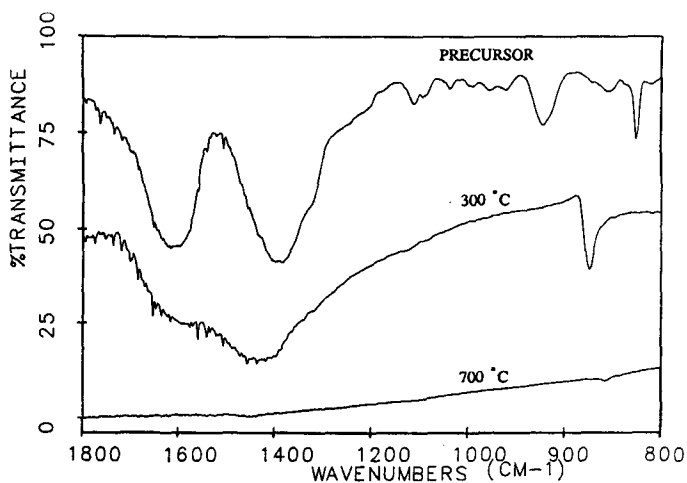


Fig. 1 FTIR data for gel precursor and products of decomposition at  $300^\circ\text{C}$  and  $300^\circ\text{--}700^\circ\text{C}$

The theoretical weight loss for the production of  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ , calculated on the basis of the stoichiometries of the metal nitrates and EDTA used, is 78.37%. This is calculated assuming that the water of crystallization of the original nitrates and EDTA is removed during the drying of the precursor. This value is very close to the experimental value of 79.4% for decomposition up to  $700^\circ\text{C}$ , calculated from the TG curve neglecting the dehydration stage.

Figure 2 also shows that the decomposition/oxidation process of the precursor in air is sharp and extremely exothermic. Therefore, to avoid vigorous heat evolution and possible segregation the precursor is calcined in two stages at  $300^\circ$  and

700°C. The powder has to be heated continuously, without cooling, to above 450°C, for the organics to decompose completely and to avoid any carbonate formation (usually SrCO<sub>3</sub> and CaCO<sub>3</sub>), by reaction with evolved CO<sub>2</sub>. As is evident from Fig. 1, carboxylate ions (–CO<sub>2</sub><sup>–</sup>), giving absorption bands at 1610, 1410, 850 cm<sup>–1</sup> [10, 11], are present in the powder calcined at 300°C and then cooled to room temperature. Once formed, decomposition of the carbonates only occurs at temperatures above 800°C, giving possible segregation and inhomogeneity in the final product. However, powder heated directly from 300° to 700°C shows no signs of carbonate formation.

### Sintering

The dilatometric data in air of the pressed pellets of the powder calcined at 700°C, are shown in Fig. 3, and indicate that up to 550°C a slight expansion occurs as a result of thermal expansion. Above this temperature a shrinkage of 13% is seen to 820±5°C as densification occurs. Between 820±5°C and 855±5°C the sample shows a linear expansion of about 3.5%. This expansion is caused by the formation of large flake-like grains of 2212 phase (5 to 15 μm) from the smaller grains of 2201 phase (1 to 2 μm). The expansion is coincident with a weight gain of 0.12% which corresponds to oxygen uptake during the phase transformation. XRD data confirm that this transformation occurs. Samples prepared at temperatures below 820°C contain mainly the 2201 phase, whereas samples prepared above 855°C show predominantly the 2212 phase.

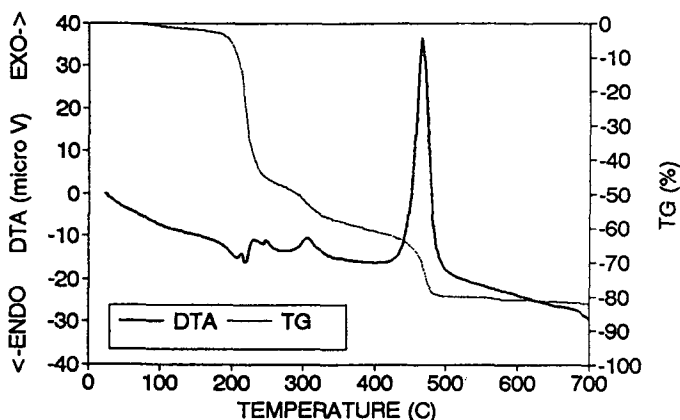


Fig. 2 TG/DTA for decomposition of precursor

### Pb-doping

The DTA traces in air of the undoped 2:2:2:3, Bi:Sr:Ca:Cu powder and for one containing Pb at 20 atomic% substitution for Bi, each show three events between

800°–900°C (Fig. 4). The curve for the undoped sample shows first a slight change in slope at 818°C, which is caused by the formation of the 2212 phase from the 2201 phase. The second and third stages can be seen as two endothermic peaks with onset temperatures of 856° and 875°C, respectively. The second stage corresponds to the partial melting of the 2212 phase (seen as a drastic shrinkage on the dilatometric curve in Fig. 3) which gives rise to the formation of Ca- and Cu-rich phases. The third stage is the decomposition of the 2212 phase to give the 2201 phase and the fusion of residual calcium cuprate. The Pb-doped curve shows the same three stages, which occur at the lower temperatures of 774°, 840° and 858°C respectively.

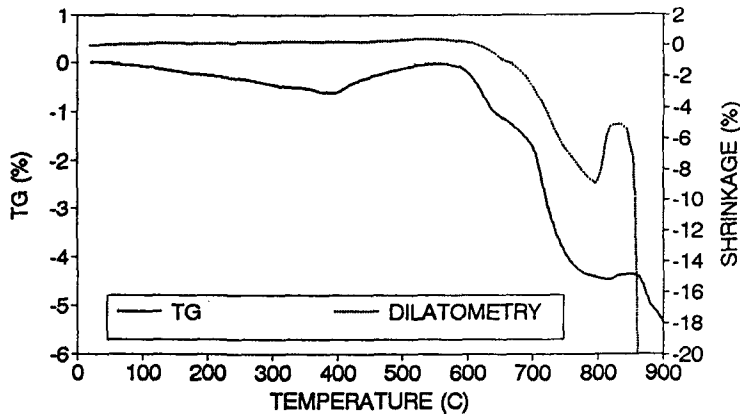


Fig. 3 Combined TG and dilatometric data for powder calcined at 700°C

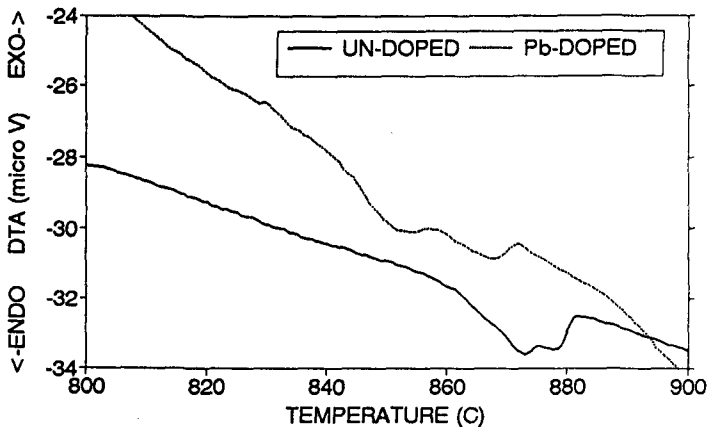


Fig. 4 DTA data for undoped and Pb-doped powder calcined at 700°C

### Oxygen partial pressure

The three stages identified previously by TG/DTA in air are also present for nitrogen/oxygen mixtures having oxygen partial pressures of 0.1, 0.15, 0.5 and 1 bar, as in Fig. 5. The third and second stages are both associated with oxygen loss, as a result of decomposition and melting respectively. Consequently, their onset temperatures both decrease as the partial pressure of oxygen is decreased. However, since the first stage is a phase transformation involving oxidation, the onset temperature of this stage increases as the partial pressure of oxygen is decreased.

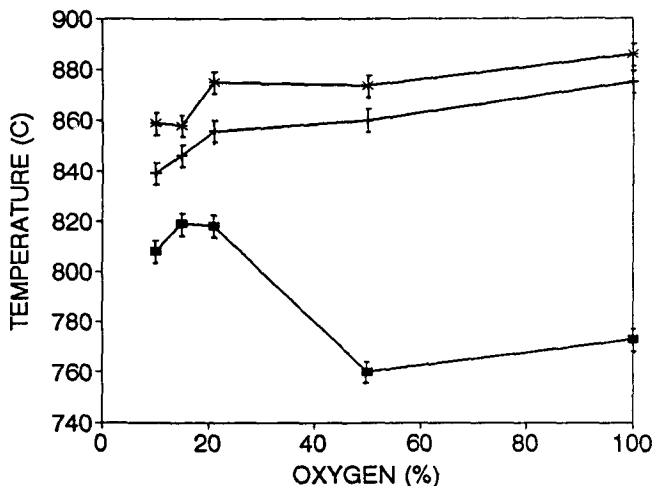


Fig. 5 Relationship between peak onset temperatures and % oxygen in the gas atmosphere

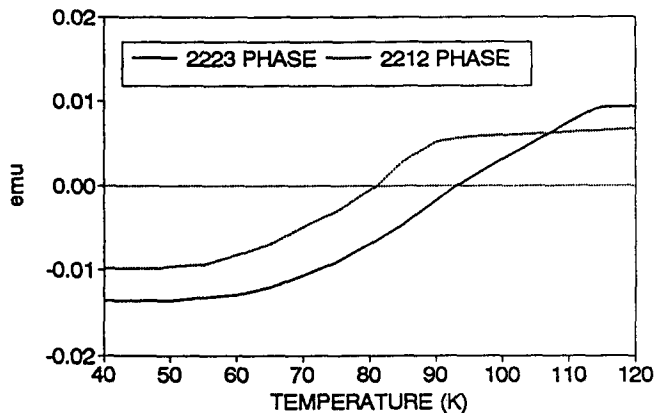


Fig. 6 Magnetic susceptibility vs. temperature relationships for undoped (2212) and Pb-doped (2223 and 2212) samples

### *Sintered sample characterization*

The onsets of the critical temperature ( $T_c$  onset) were investigated in a vibrating sample magnetometer (VSM). (Because of an unknown residual magnetic field present in the equipment used the complete superconductive transition is broadened.)

The samples containing the 2212 phase sintered for 1 hour at different temperatures have a  $T_c$  onset of 94 K. On holding the Pb-doped sample at 850°C, in air for 100 hours, it developed a large amount of 2223 phase with an  $T_c$  onset of 112 K (Fig. 6). This holding temperature is within the range of partial melting, and the liquid originally having a composition of 2212 gradually becomes enriched in Ca-Sr and Cu to produce the 2223 phase. Study of the samples containing the 2223 phase by STA shows that the partial melting temperature is lower for these samples than for the samples containing the 2212 phase and indicates the importance of the liquid phase in 2223 phase formation.

### **Conclusions**

1) Decomposition of the EDTA gel precursor for BSCCO superconductors has to be controlled closely to avoid the formation of carbonates.

2) During the 2201 → 2212 phase transformation, expansion of the sample occurs because of large lattice parameter changes and the flaky growth of the 2212 phase.

3) The 2223 ( $T_c = 110$  K) phase is only obtained with long periods of sintering compared to those necessary for the easily achievable 2212 ( $T_c = 90$  K) phase.

4) The higher stability of the 2212 phase makes possible the following decomposition reaction for the 2223 phase



5) The reduction in the phase formation and melting temperatures of Pb-doped samples as well as the effects caused by sintering in low oxygen partial pressures both indicate the necessity of the liquid-phase-aided reaction for formation of the 2223 phase.

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**Zusammenfassung** — Mittels STA (TG/DTA) und Dilatometrie wurde in Verbindung mit FTIR die Zersetzung von EDTA Gelpräkursoren für die Fertigung von BSCCO Supraleitern untersucht. Die thermoanalytischen Daten wurden unter dem Aspekt der Abfolge der Phasenbildungsprozesse diskutiert, welche für die Herstellung der supraleitenden Phase 2223 BSCCO notwendig ist. Auch der Einfluß des Ersatzes von Bi durch Pb bei den Temperaturen für die Bildung der supraleitenden Phase wurde diskutiert. STA wurde auch bei verschiedenen Partialdrücken für Sauerstoff durchgeführt, um den Einfluß des Sauerstoffdruckes auf die Bildung und Zersetzung der bei der Herstellung der Verbindung 2223 auftretenden Phasen zu bestimmen.