

THERMOANALYTICAL STUDIES OF THE PROCESSING OF BULK AND THIN FILM BSCCO HIGH T_c SUPERCONDUCTORS BY THE EDTA-GEL ROUTE

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Abstract

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.

Thin film preparation of Bi-based high T_c superconductors have been carried out on MgO (100). Grain orientation of oxide thin films has been investigated. Well orientated 2212 grains have been achieved, with the (001) planes parallel to the substrate.

The EDTA-gel method has been modified by the addition of glycerol to achieve the appropriate viscosity for spin coating. STA has been used to study the decomposition of these modified gels for the formation of thin films.

Keywords: dilatometry, superconductors, TG/DTA

Introduction

At least three superconductive phases which can be characterised by the number of CuO planes (n) in their perovskite crystal structure exist in the $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n+\delta}$ system. The 2201 phase ($n = 1$), which was first found by Michel *et al.* [1] has a $T_c \approx 10$ K and a lattice parameter of $c = 24.6$ Å. The other two phases were discovered by Maeda *et al.* [2]. The 2212 phase ($n = 2$) with $T_c = 90$ K and 2223 phase ($n = 3$) with $T_c = 110$ K have lattice parameters of $c = 30.9$ Å and $c = 37$ Å, respectively.

Schulze *et al.* [3] have shown that in the phase diagram the single phase region of the 2223 phase is very small compared to those of the 2212 and 2201 phases and hence explained the reason why the 2201 and 2212 phase are relatively easier to prepare compared to the 2223 phase. Takamo *et al.* [4] found that Pb-doping increased the volume fraction and stabilised the desired 2223 phase.

The complex composition of the 2223 phase has made it necessary to seek alternative preparative techniques to overcome the problems of inhomogeneity and contamination associated with the conventional ceramic processing method using oxide or oxide/carbonate mixtures and repeated firing and subsequent grinding operations. In this study the EDTA-gel route is used to obtain a precursor of high chemical homogeneity which is subsequently decomposed to give the final product.

While the production of bulk samples of high temperature superconductors is important for the construction of wire and ribbon conductors, the production of high-quality films with uniform thickness on non-reactive substrates with matching coefficient of thermal expansion is essential for a wide variety of electronic applications, such as SQUIDS (Superconducting Quantum Interference Devices), resonators, ac/dc converters, band-pass filters and ultimately super computers [5]. Dip coating and spin coating using gels are very effective in depositing uniform and pure complex oxides at low temperatures [6]. However, for EDTA-based gels to be used in such coating processes control of viscosity needs to be achieved. To do this either ethylene glycol or glycerol can be added to the gel. However, once either of these is added the thermal stability of the gels is likely to be altered. As a result, a major part of the present paper is to compare thermoanalytical data for gels used to produce particulate material with those obtained for modified gels used in the production of thin films. The modification used for these samples was the addition of glycerol.

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 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 NH_4OH solution. The solution was dehydrated to form the amorphous precursor using a rotary evaporator and a vacuum oven [7–9].

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 in various oxygen partial pressures (100 ml/min flow rate). Subsequently, for bulk sample preparation the precursor was calcined in two stages at 300 and 700°C. After ball milling the calcined powders were pressed into pel-

lets (3.5 mm d., 4 mm. h) using pressure of $370 \text{ MN}\cdot\text{m}^{-2}$. The sintering behaviours of the pellets were determined using dilatometry, with a sensitivity of $\pm 5 \times 10^{-6} \text{ m}$, in flowing air. Heating rates of $3\text{--}10 \text{ deg}\cdot\text{min}^{-1}$ were used.

For thin films containing glycerol sample gels were taken directly from the rotary evaporator, thus by-passing the vacuum oven drying operation, and placed into sample containers for thermal analysis. In addition, thermal analysis was also carried out on glycerol, EDTA and a 3:1 mixture (glycerol:EDTA) to give data for assistance in the explanation of the results obtained for the gels.

Thin film preparation

As in the precursor production for thin films the high purity metal nitrates were dissolved in deionised water. Ultimately the molar ratio of metal nitrates:EDTA:glycerol was kept in the ratio 1:1:1 to achieve the correct viscosity and decomposition conditions as well as ensuring the presence of enough acid. The *pH* of the solution was kept at 6. The solution was partially dehydrated to form a viscous gel using a rotary evaporator. Gels were produced with varying glycerol additions to study the effects of glycerol on viscosity and on the thermal stability of the gel. The gel was poured over the polished MgO (100) substrate, 1 cm^2 , in the required quantity and spun at a speed of 2000–4000 rpm to form thin layers. It was transferred to an oven set at 80°C and left overnight to dehydrate and form a firm polyester layer.

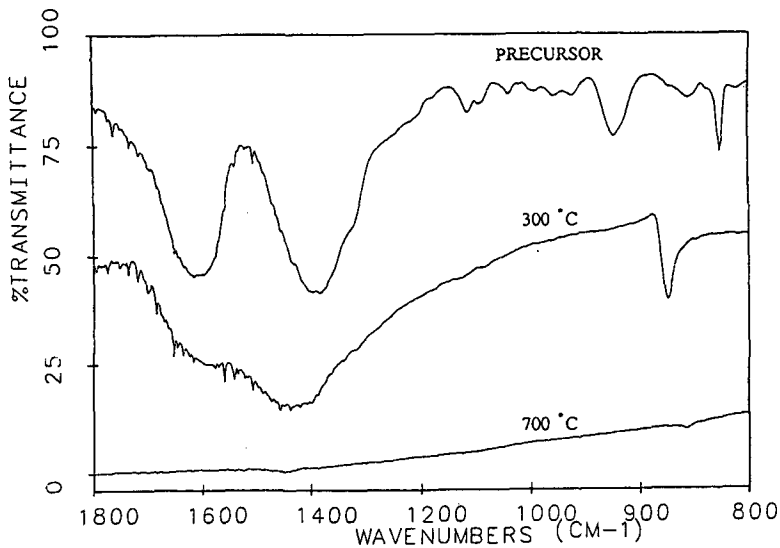


Fig. 1 FTIR data for gel precursor and products of decomposition at 300°C and $300\text{--}700^\circ\text{C}$

The samples were later transferred to a cylindrical furnace and sintered at appropriate temperatures obtained from thermal analysis data in flowing air.

Materials characterisation

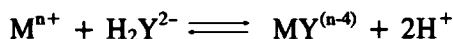
The precursor and oxide products were characterised by XRD using $\text{CuK}\alpha$ radiation and a Philips diffractometer. The composition of the phases in the sintered samples were identified by EDX analysis and SEM. Critical temperature onsets were determined in an Oxford Instrument Vibrating Sample Magnetometer (VSM) and a resistance-measurement apparatus. FTIR was used to characterise the precursors and products obtained after heating to various important temperatures indicated by thermal analysis.

Results and discussion

Bulk particulate materials

Precursor formation and decomposition

The formation of the organometallic precursors depends on *pH*. In neutral to moderately basic solution EDTA combines with metal ions in a 1:1 ratio [10] as:



where Y refers to EDTA.

The 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 cm^{-1} absorption refers to antisymmetrical stretching of carboxylate groups $-\text{COO}^-$ which are acid groups binding metal ions [11–12].

Simultaneous TG/DTA data for the decomposition of the precursor are given in Fig. 2 where three stages can be identified. The first stage is dehydration taking place between $50\text{--}150^\circ\text{C}$. The second stage, between 150 and 400°C , is the initial decomposition of the organic-nitrate complex which gives rise to the evolution of H_2O , CO_2 and nitrous oxide. The third stage is the final decomposition of the precursor between $400\text{--}500^\circ\text{C}$ with the further removal of organic materials as CO_2 and H_2O along with some NO_2 are evolved from the carbonaceous char produced on heating the gel to 400°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 crystallisation 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°C, calculated from the TG curve neglecting the dehydration stage.

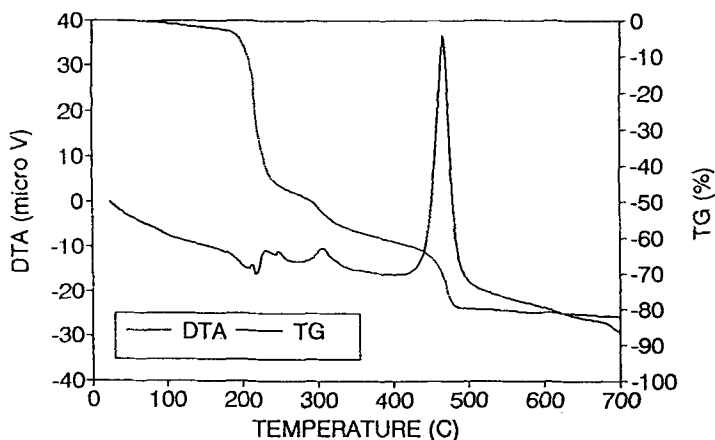


Fig. 2 TG/DTA for decomposition of precursor

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 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_3 and CaCO_3), by reaction with evolved CO_2 . As evident from Fig. 1 carboxylate ions ($-\text{CO}_2^-$) giving absorption at 1610, 1410, 850 cm^{-1} bands [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 linear shrinkage of 13% is seen on heating to $820 \pm 5^\circ\text{C}$ as densification occurs. Between $820 \pm 5^\circ\text{C}$ and $855 \pm 5^\circ\text{C}$ the sample shows a linear expansion of about 3.5%. This expansion is caused by the formation of large flake-like grains of the 2212 phase (5 to 15 μm) from the smaller grains of the 2201 phase (1 to 2 μm).

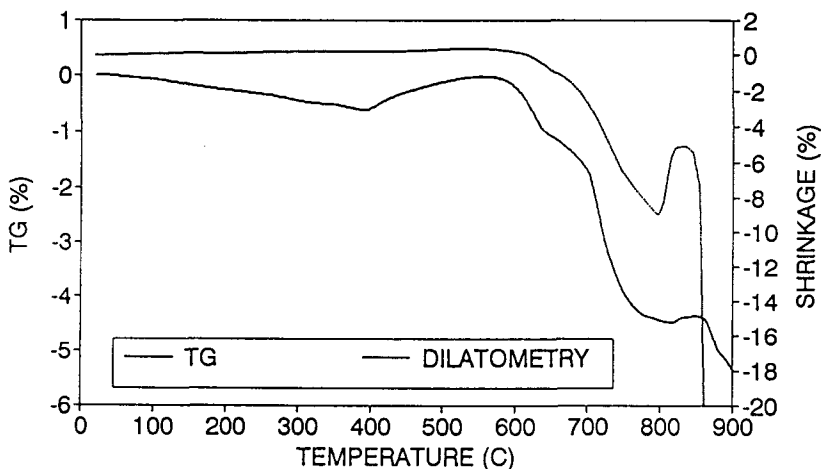


Fig. 3 Combined TG and dilatometric data for powder calcined at 700°C

The expansion is coincident with a weight gain of 0.12% which is the oxygen uptake during the 2212 phase formation. XRD data confirm the 2212 phase formation occurs. Samples prepared at temperatures below 820°C contain mainly the 2201 phase whereas samples prepared above 855°C show the predominant existence of the 2212 phase. Subsequent work on the effects of Pb doping [13] has shown the production of the 2223 phase via a liquid phase aided reaction.

Thin film preparation

Thin film formation and characterisation

As indicated earlier, to be able to achieve a uniform layer on a polished MgO (100) substrate control of the viscosity of the gel is required. If the viscosity is too low the gel will just run off the substrate and if it is too high the gel will not form a thin film on the substrate. The method used to control viscosity was the addition of glycerol during gel production. The appropriate viscosity control was found to be achieved at a molar ratio of glycerol:EDTA of 1:1. Figure 4 shows the STA data obtained on heating such a gel over the temperature range room temperature to 600°C. The data are quite similar to those presented in Fig. 2 for the glycerol-free gel with the minor differences of the smoothing out of the multi-stage nature of the first decomposition event and the production of a two-stage decomposition of the carbonaceous char at 450°C.

Figure 5 shows the DTA data obtained for glycerol, EDTA and molar ratio of glycerol:EDTA of 3:1. Glycerol decomposition occurs at about 200°C and is

seen as an endothermic peak. EDTA decomposes in two stages, first at about 200°C which is an endothermic event and secondly an exothermic peak can be seen at around 450°C. The mixture of glycerol and EDTA shows that the endothermic event at about 200°C is still present. However, the exothermic peak is broadened and a two stage decomposition is noticeable. This arises from the polymerisation of glycerol and EDTA where no other species are present.

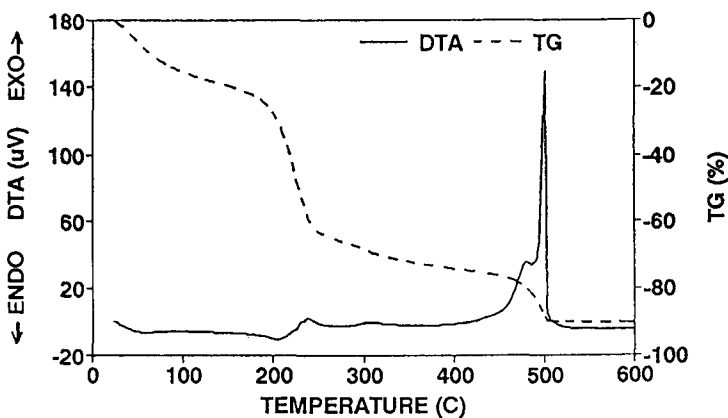


Fig. 4 TG/DTA for decomposition of gel precursor containing a glycerol:EDTA ratio of 1:1

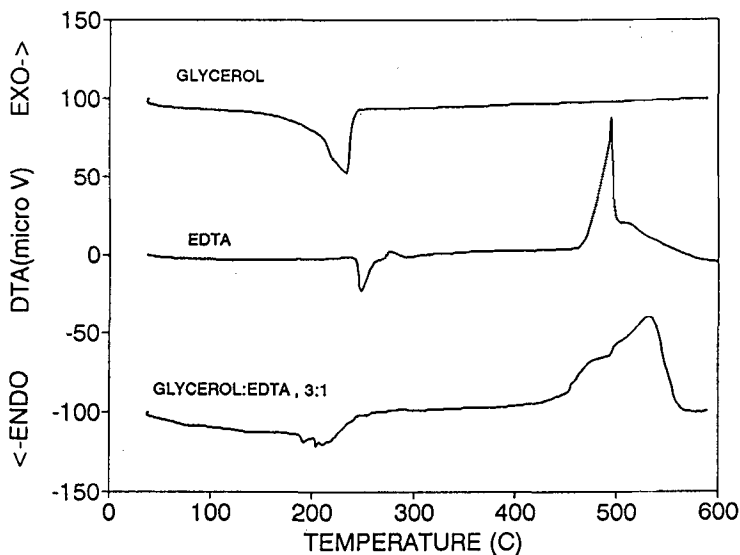


Fig. 5 DTA data for decomposition on heating of glycerol, EDTA and a mixture of ratio 3:1, glycerol:EDTA

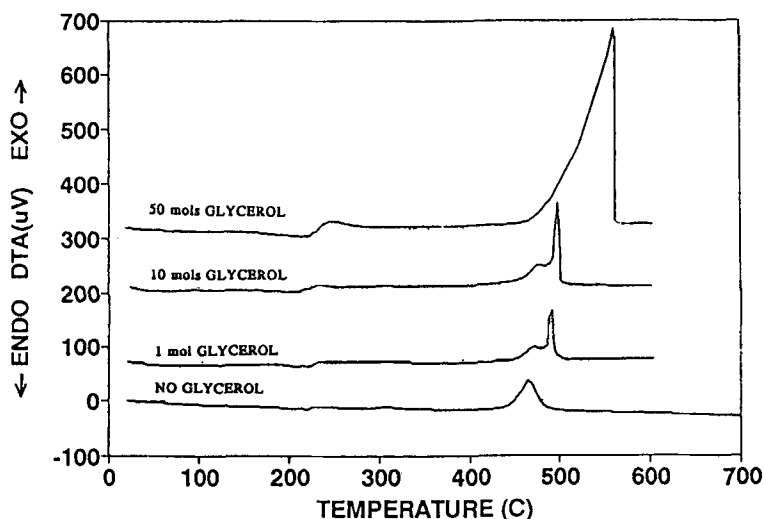


Fig. 6 DTA data for gels containing differing quantities of glycerol

Figure 6 shows the decomposition behaviour of the gels containing different molar ratios of glycerol:EDTA studied by DTA. The higher quantities of glycerol, which increase the viscosity of the gel, can be seen to increase the heat evolution during decomposition, particularly in the temperature region 450°C and above. Little change occurs to the thermal stability of the gels in the lower temperature regions of 200°C and above where gel decomposition begins. As indicated before, the effect of glycerol is only to 'smooth out' the multi-stage decomposition of the gel in the region 250 to 300°C . This effect is demonstrated by a comparison of Fig. 2 for the gel containing no glycerol and Fig. 4 for the gel of glycerol-EDTA ratio of 1:1. The mass changes over this temperature range are similar for both glycerol-free and glycerol-containing gels with slightly higher values being obtained for glycerol-containing samples. At temperatures below 200°C the extra mass loss seen for the glycerol-containing gels is associated with water loss as these gels are less well dried as they are not processed through the high vacuum oven. Similarly, the mass changes associated with the large exothermic event at 450 to 500°C are also similar, with a proportionately increasing mass change associated with the residual carbon char being associated with gels containing larger amounts of glycerol.

It is thus apparent that the glycerol is combined within the polymerised gel and is involved in the decomposition process. Its main effect, however, is the production of extra free carbon in the char which contributes massively to the exothermic oxidation process at temperatures in excess of 450°C . An added complication is that this final decomposition/oxidation process is initially two-

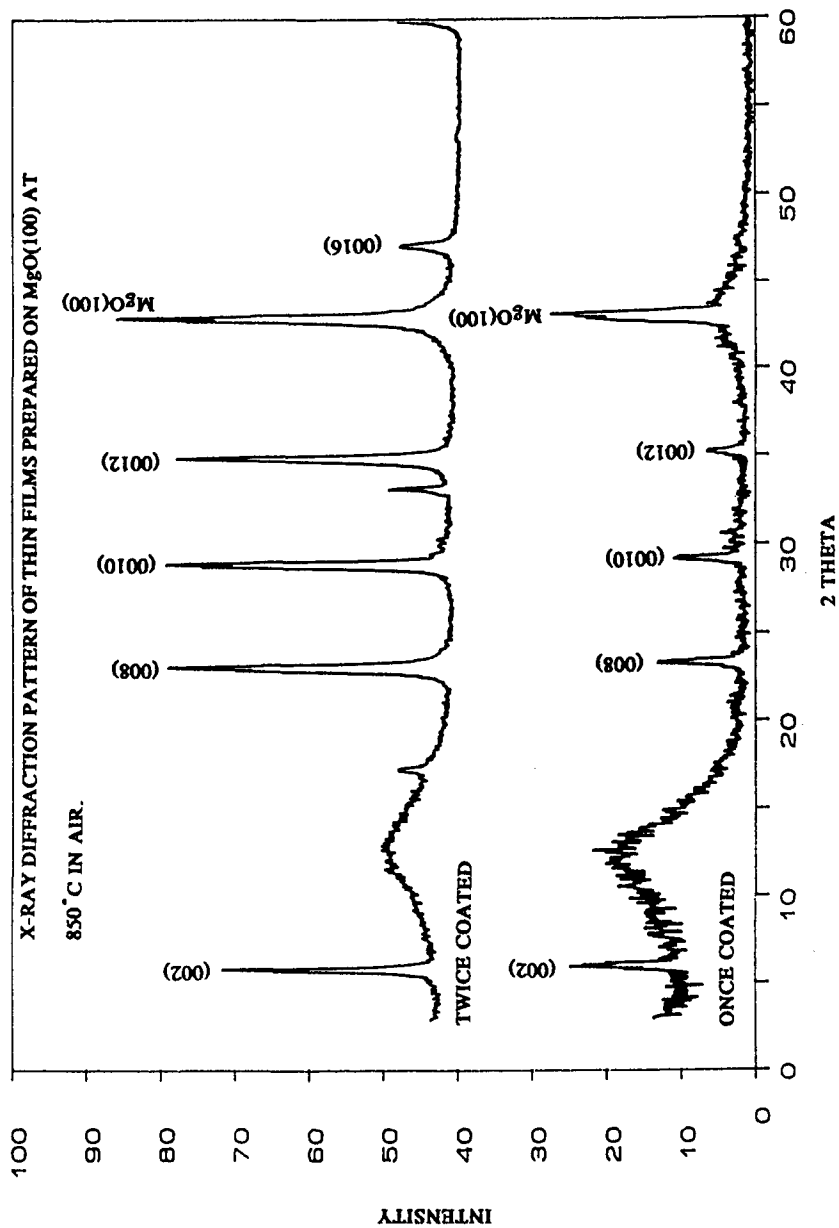


Fig. 7 XRD data for thin films prepared on MgO (100) substrates at 850°C in air

stage and then is extended over a larger range of temperature, (as indicated in Fig. 6) where it can be seen that the process is not completed until a temperature of 550°C for the gel containing 50 mol glycerol.

Sintering and characterisation

Figure 7 shows the XRD traces of the thin films sintered at 850°C in air for 1 h. The traces reveal the formation of the 2212 phase where only the (001) Bragg diffraction peaks of the 2212 phase are present. A second coating increases the thickness of the film and hence the intensity of the diffracted peaks. The growth of the 2212 phase with *ab*-planes parallel to the substrate surface was also clearly evident in SEM micrographs. The transition temperatures of the films have been studied by resistivity measurements. Preliminary data give transition temperatures of about 78 K compared to the bulk samples of the 2212 phase being 90 K. This variation in T_c value is presently being studied, however, it is believed to be possible because of oxygen stoichiometry of the phases present [14]. The microstructural aspects of the growth of the thin films and the dependence of T_c upon microstructure and composition will be the subject of a future communication.

Conclusion

1. The decomposition of the precursor occurs in three stages, which are accompanied by large heat effects and associated mass changes.
2. Controlled calcining is required to avoid the formation of carbonates.
3. The formation of the 2212 phase from the 2201 phase along with an expansion in volume of samples.
4. Gels prepared for thin film production with the incorporation of glycerol are subject to extra self-heating particularly in the final stages of oxidation/decomposition of the carbonaceous char. The extent of self-heating is dependent upon the quantity of glycerol added to control viscosity.
5. Thermoanalytical data indicate that the glycerol is chemically combined within the gels prepared for thin film production.

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Zusammenfassung — Mittels STA (TG/DTA) und Dilatometrie in Verbindung mit FTIR wurde die Zersetzung von EDTA Gelpräkursoren für die Herstellung von BSCCO Supraleitern untersucht. Die thermoanalytischen Daten wurden unter dem Aspekt der Reihenfolge der Phasenbildung diskutiert, die für die Bildung der supraleitenden Phase 2223 BSCCO erforderlich ist. Die Herstellung des Filmes von Hoch- T_c Supraleitern auf Bi-Basis erfolgte auf MgO (100). Die Kornausrichtung der dünnen Oxidfilme wurde untersucht. Es wurden gutausgerichtete 2212 Körner mit der (001) Ebene parallel zum Substrat erhalten. Die EDTA Gelmethode wurde durch den Zusatz von Glycerol modifiziert, um eine ausreichende Viskosität für das Schleuderbeschichten zu erhalten. STA wurde zur Untersuchung der Zersetzung dieser modifizierten Gele für die Bildung von dünnen Filmen verwendet.