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SYNTHESIS AND CHARACTERIZATION OF HIGH TEMPERATURE SUPERCONDUCTORS

System Bi–Pb–Sr–Ca–Cu–O

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Abstract

The high temperature superconductors of the system Bi–Pb–Sr–Ca–Cu–O show promising properties and large scale applications can be considered. The $(Bi,Pb)_2Sr_2Ca_2Cu_30_{10+\delta}$ (Bi,Pb(2223)) phase is attractive because of its high superconducting temperature (110 K) and high current transport capabilities.

Simultaneous DTA/TG has proved an excellent tool for synthesizing, characterizing these high temperature superconductors, confirming phase diagrams and finding the optimal annealing temperature for Bi,Pb(2223)/Ag tapes in order to obtain high critical current densities around 30 kA cm^{-2} at 77 K and 0T. The identification of the main DTA peaks of measurement of different phase mixtures made it possible to observe the formation of an intermediate phase Bi,Pb(2212) during the formation of Bi,Pb(2223).

Keywords: high-temperature superconductors, superconductors

Introduction

Since the discovery of superconductivity in the Bi–Pb–Sr–Ca–Cu–O system [1], the $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$(Bi,Pb(2223)) phase has attracted a lot of attention because of the high superconducting transition temperature ($T_c=110$ K) and because of its high current transport capabilities. For example, Bi,Pb(2223) silver sheathed tapes can be used for high magnetic fields above 25 *T* and for carrying large current densities in a variety of temperature ranges. Despite the promising capabilities of this phase, some difficulties still remain. The reaction path to the formation of Bi,Pb(2223) is still not completely understood. This is in part due to the very small stability domain added to the fact that the stoichiometric composition is not included in this domain [2]. In addition, the optimal conditions to obtain high critical current densities in silver sheathed Bi,Pb(2223) tapes are still not elucidated.

Simultaneous DTA/TG measurements have been used to study the formation of Bi,Pb(2223). The secondary phases have also been studied and characterized using this technique in order to obtain a global view of the Bi–Pb–Sr–Ca–Cu–O system.

Bi,Pb(2223) silver sheathed tapes have been studied to find the optimal preparation conditions for obtaining high critical current densities.

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Experimental

In order to have a picture about the phases present and about the formation mechanisms, different precursor powders were used. Some $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi(2212)) and Bi,Pb(2223) phases were commercially purchased from Hoechst AG for a first approach to the system. Most phases analyzed in the present study were prepared from oxides and carbonates (Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, CuO) with the correct stoichiometry. Pb substitution has been used because it facilitates the formation of Bi,Pb(2223) [3–5]. Subsequently, Bi,Pb(2223) silver sheathed tapes were prepared using the following procedure:

1) Coprecipitated powders of nominal composition $Bi_{1.72}Pb_{0.34}Sr_{1.83}Ca_{1.97}Cu_{3.13}O_{10+\delta}$ were first precalcined around 300°C.

2) These powders were calcined 2 to 3 times at 820°C composed mainly of Bi(2212), Ca_2PbO_4 and CuO.

3) The resulting precursor powders are then introduced into a silver tube and deformed to obtain the tape form.

4) Finally, the tapes are annealed for the transformation to Bi,Pb(2223) in order to obtain high critical current densities [6].

All samples were analyzed by Differential Thermal Analysis with simultaneous thermogravimetry on a SETARAM TAG 24. The heat treatment temperatures were determined either by using existing phase diagrams or by choosing a temperature range just below the main decomposition or melting peak on DTA measurements.

The operating parameters for the DTA/TG apparatus were the following:

The samples were ceramic oxides of the system Bi–Pb–Sr–Ca–CuO in the form of precursors or the final phases with a mass between 50 mg and 100 mg. The crucibles used were almost exclusively Al_2O_3 without cover. For comparison purposes, platinum crucibles were used. The atmosphere was either flowing artificial air, or flowing argon. The heating rate was always $\beta = 2°C\ min^{-1}$. The reference used was calcined Al_2O_3. The Pt/PtRh 10% thermocouples are situated underneath the crucibles.

Additional identification of the phases present were performed using X-ray diffraction (XRD) on a Θ–2Θ Philips 1820.

Results and discussion

Characterization of secondary phases

The Ca_2CuO_3 phase is often encountered in the precursor powder when preparing Bi,Pb(2223). The DTA curve of this phase is shown in Fig. 1. The measurement is given with rising temperature until 1100°C under flowing air and decreasing at a rate β of $2°C\ min^{-1}$. When increasing the temperature, there appears an endothermic peak with an onset temperature T_{on} at 1030°C. When decreasing the temperature, there are 3 endothermic peaks with T_{on} of 1030, 1013 and 995°C.

These results agree well with the results of Gadalla and White [7] and Roth *et al.* [8] except for the peak at 995°C that is situated at different temperatures in the diagrams found in the literature. This peak is probably due to a contamination by the Al_2O_3 crucible that can influence the measurement. Indeed, in the oxide systems, the method of determining the phase diagrams by going above the melting temperature and noting the temperatures upon cooling can only be used with precaution because of the great reactivity of the oxides with the Al_2O_3 crucibles. One has to mention also that the DTA/TG of CaO–CuO is difficult because the produced liquids escape easily from the crucible.

The Ca_2PbO_4 phase plays an essential role in the formation of Bi,Pb(2223). It is formed in the precursors when they are calcined and it disappears during the formation of Bi,Pb(2223) [9]. Figure 2 shows the DTA measurement of this phase under flowing air. Upon heating, Ca_2PbO_4 decomposes at 980°C. This temperature corresponds to the formation of a liquid phase in the phase diagram of PbO–CaO by Kitaguchi *et al.* [10]. Above this temperature, we have CaO and a liquid. We have also performed a DTA measurement of a mixture of Ca_2PbO_4 and PbO to study the Pb-rich domain of the phase diagram. The corresponding DTA measurement is also given in Fig. 2. There is a first endothermic peak corresponding to the transformation of Pb_3O_4 (sometimes formed during grinding) into PbO, and a second endothermic peak at 846°C. This measurement confirms the phase diagram established by Kitaguchi *et al.* [10]. Our results do not confirm the phase diagram determined by Kuxmann and Fischer [11] showing a liquid formation temperature of 822°C. A possible explanation might be that these authors have performed their analysis under argon.

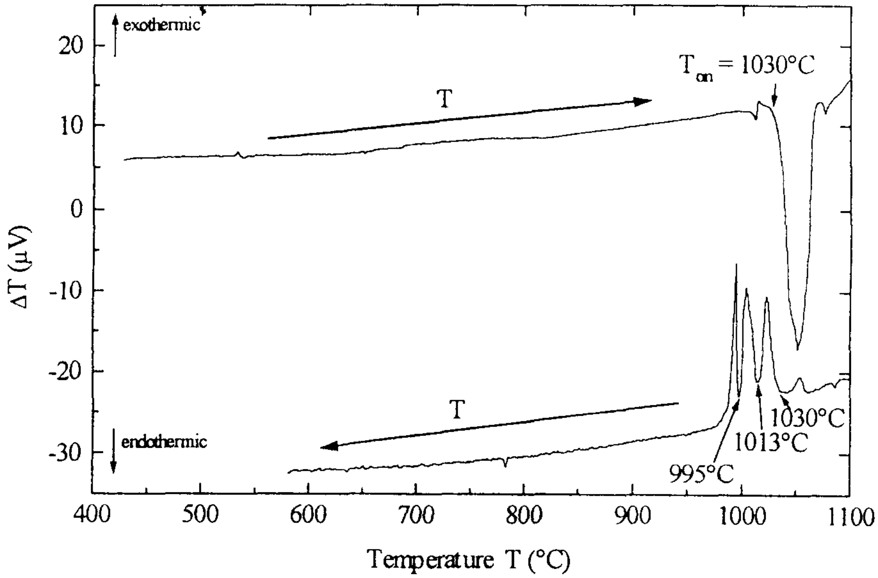

Fig. 1 DTA measurement of Ca_2CuO_3 in flowing artificial air at 2°C min^{-1} upon heating up to 1100°C and cooling down

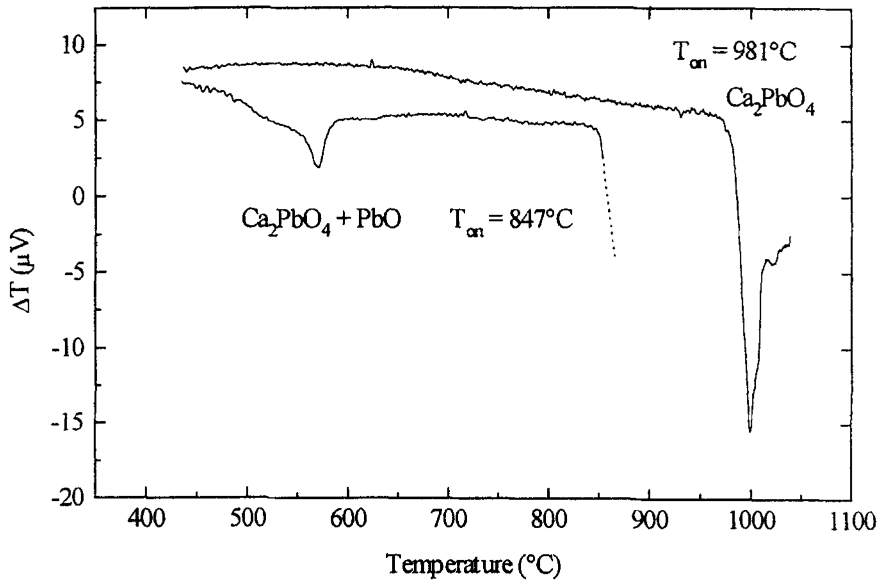

Fig. 2 DTA measurement of Ca_2PbO_4 and Ca_2PbO_4+PbO under flowing artificial air.Only the heating section of the measurement is shown

Table 1 Onset temperature of main endothermic peak of the secondary phases present in the Bi–Pb–Sr–Ca–Cu–O system

Secondary phases of the Bi–Pb–Sr–Ca–Cu–O system	T_{on} of the main endothermic peak of DTA measurement upon heating/°C
Bi_2O_3 [21]	825
PbO [21]	886
SrO [21]	2430
CaO [21]	2580
CuO [21]	1236
Ca_2PbO_4	980
Ca_2CuO_3	1030
$CaSr_2Cu_5O_8$	972
$Bi_2(Sr,Ca)_3O_x$	670

We have studied many other secondary phases of the system we synthesized, pure and as phase mixtures. The onset temperatures of the main endothermic peak are given in Table 1.

Most phases melt at temperatures above 860°C, a temperature at which Bi,Pb(2223) is still synthesized. Bi_2O_3 melts at a lower temperature (825°C) but has usually already reacted and is absent in the Bi(2212) containing precursor mixtures. As for the $Bi_2(Sr,Ca)_3O_x$ phase, it appears in samples prepared in an oxygen-reduced atmosphere but is absent in air under the conditions at which Bi,Pb(2223) is synthesized. It follows that these two secondary phases cannot be responsible for the endothermic peaks observed in DTA measurements between 800 and 890°C.

Characterization of the main superconducting phases

We have also studied the high critical temperature superconducting phases, namely, Bi(2212) and Bi,Pb(2223). From the literature, we know that the Bi(2201) phase has an onset temperature T_{on} around 900°C [12].

Figure 3 shows the DTA measurement for the Bi(2212) phase from Hoechst AG under flowing synthetic air in a platinum crucible. The choice of this crucible for the measurement was justified by the strong reaction observed with Al_2O_3 and the liquid above 900°C. However, the onset temperature of 884°C is the same for Al_2O_3 and platinum crucibles.

Figure 4 shows the DTA measurement for Bi,Pb(2223) under flowing air in both a platinum and Al_2O_3 crucible. Both curves show the same characteristics except for the difference in base line resulting from the difference in specific heat of the sample holders used. The onset temperatures of 876°C are the same for both crucibles. This temperature is about 8°C lower than the one for Bi(2212) presented above. This difference makes it easier to identify endothermic peaks in DTA measurements made on mixtures and precursor powders.

Figure 5 shows the DTA measurement for two types of precursor powders, with and without Pb. These precursor mixtures are mainly composed of Bi(2212),

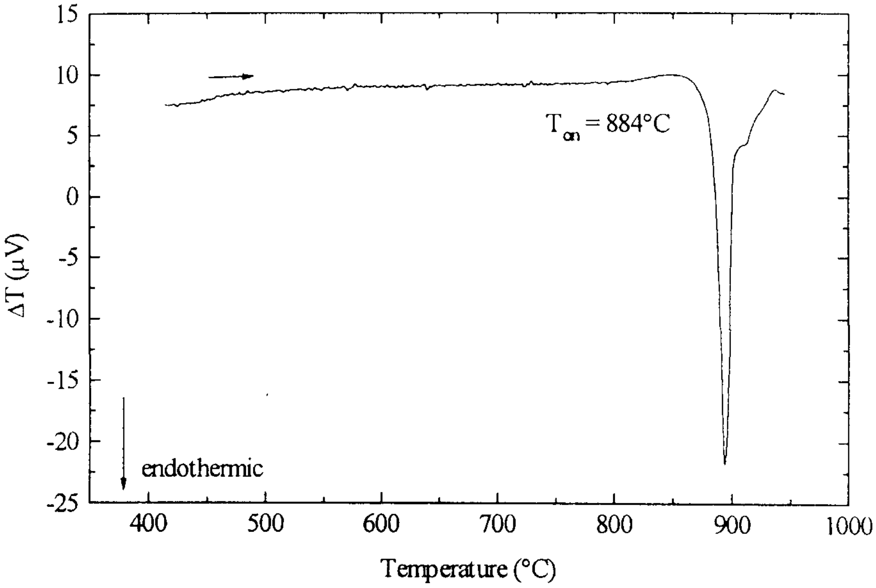

Fig. 3 DTA measurement of Bi(2212) at 2°C min^{-1} under flowing air in a platinum crucible in order to avoid reaction with an Al_2O_3 crucible

Ca_2PbO_4 (in the case of Pb containing powders), Ca_2CuO_3 and CuO. In Fig. 5, the onset temperature of 884°C of the Pb-free powder corresponds well with the onset temperature of Bi(2212) presented in Fig. 3, the other secondary phases melting at

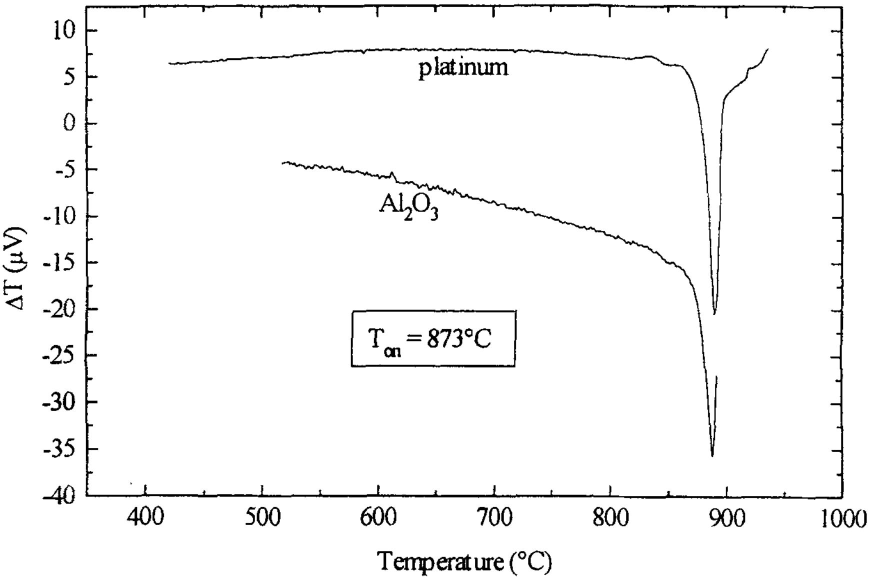

Fig. 4 DTA measurement of Bi,Pb(2223) at 2°C min^{-1} under flowing air in a platinum and Al_2O_3 crucible

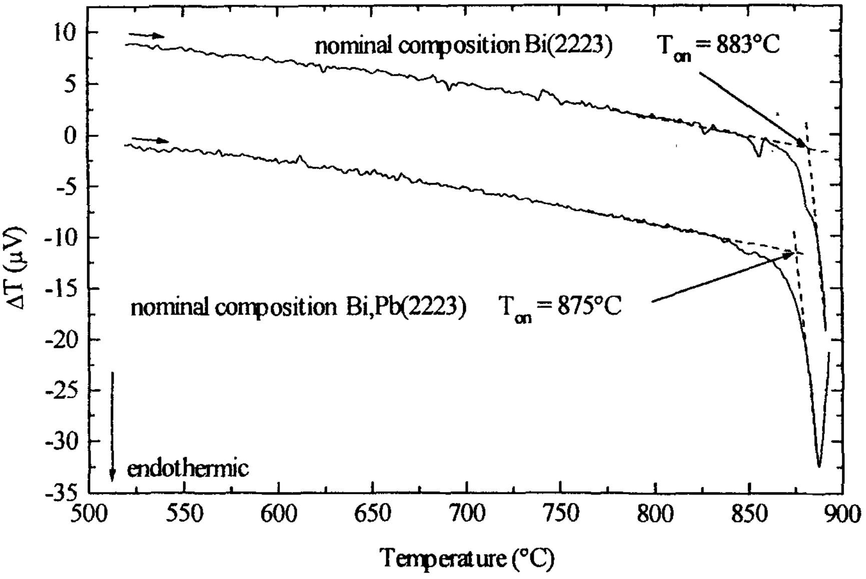

Fig. 5 DTA measurement of two calcined precursor powders with nominal composition Bi(2223) and Bi,Pb(2223) under flowing air at 2°C min^{-1}

much higher temperatures. In the case of the Pb containing powder, the onset temperature is about 8°C lower and corresponds to the onset temperature of Bi,Pb(2223) presented in Fig. 4. One can be tempted to attribute this onset temperature to the decomposition of the Bi,Pb(2223) phase. However, the transformation kinetics for the formation of this phase are very slow [13].

Consequently, there is not enough time during a DTA run at 2°C $\min^{-1}$ for the transformation from the precursors to Bi,Pb(2223) to take place. Thus this DTA peak must correspond to another phase. We have attributed it to the Pb containing Bi(2212) phase noted Bi,Pb(2212) [13]. Indeed, this intermediate phase is formed when preparing Bi,Pb(2223) [14]. The identification of this phase was confirmed by our study as can be seen from Table 2 showing the onset temperatures of the main endothermic peak of the superconducting phases and some mixtures with secondary phases. The nominal composition of the mixtures was chosen as $Bi_{1.72}Pb_{0.34}Sr_{1.83}Ca_{1.97}Cu_{3.13}O_{10+\delta}$ as long as the elements present permitted.

It can be seen from Table 2 that most phase mixtures containing Bi(2212) have T_{on} of the main peak lowered from 884 to around 870°C, the lowest T_{on} (867°C) being for a mixture of Bi(2212) and CuO. Holesinger *et al.* [15] have shown that the appearance of a liquid observed by the presence of an extra endothermic peak tends to lower the melting point of Bi(2212), more precisely, the T_{on} of the main peak. They studied different compositions and when there was no extra peak, T_{on} varied between 885 and 900°C. However, when a second peak appeared before the main peak, T_{on} varied between 870 and 883°C.

Their observations agree with our results: if we add Ca, Cu, Pb or Bi rich phases to Bi(2212), T_{on} is lowered from 884 to 870°C.

Table 2 Onset temperature of main endothermic peak of mixtures containing Bi(2212) and Bi,Pb(2212)

Phase mixture containing Bi(2212) or Bi,Pb(2212)	T_{on} of main endothermic peak/°C
Bi(2212)	884
Bi,Pb(2223)	876
$Bi_{2-x}Pb_xSr_2CaCu_2O_{8+\delta}$ (x=0.2)	878
$Bi_{2-x}Pb_xSr_2CaCu_2O_{8+\delta}$ (x=0.4)	876
$Bi_{2-x}Pb_xSr_2CaCu_2O_{8+\delta}$ (x=0.6)	873
0.86Bi(2212)+0.34Ca_2PbO_4	871
0.86Bi(2212)+$CaCO_3$	870
0.86Bi(2212)+0.34PbO	875
0.86Bi(2212)+0.5Ca_2CuO_3	877
0.86Bi(2212)+$CaSr_2Cu_5O_8$	880
0.86Bi(2212)+CuO	867
Bi,Pb(2212)+CuO	860
Bi,Pb(2212)+0.5Ca_2CuO_3	875
Bi,Pb(2212)+CuO+Ca_2CuO_3	873

The fact that the latter temperature is close to the decomposition temperature of Bi,Pb(2223) could signify that the formation of this phase necessitates Bi(2212) and a liquid. This liquid brings the necessary elements like Ca and Cu to the reaction. Pb which is an element playing an essential role in our system is favorable for the formation of the liquid. The presence of this liquid and the shape of the DTA/TG curves indicate that Bi(2212) forms a eutectic with phases containing Ca, Cu or Pb.

Synthesis of new superconducting phases

For the synthesis of phases under the solid-state regime the formation temperature is chosen just below T_{0n} of the main endothermic peak. In some cases where multiple peaks occur, as can be expected for a mixture of phases in precursor powders, the synthesis temperature is still chosen before the main peak, but after one of the preceding endothermic peaks. As a result, some partial melting occurs during the synthesis, facilitating the phase formation. As an example, we will discuss the formation of the superconducting phase: Bi,Pb(2212). This phase appears as an intermediate step upon heating precursors when forming Bi,Pb(2223) [14]. Starting from precursor powders composed of Bi(2212), Ca_2PbO_4 and CuO, upon heating, we first form Bi,Pb(2212) by a change in composition during a rapid reaction. Subsequently, Bi,Pb(2223) is slowly formed [9, 16]. The DTA has been useful for determining the optimal synthesis conditions. In the literature, this phase was synthe-

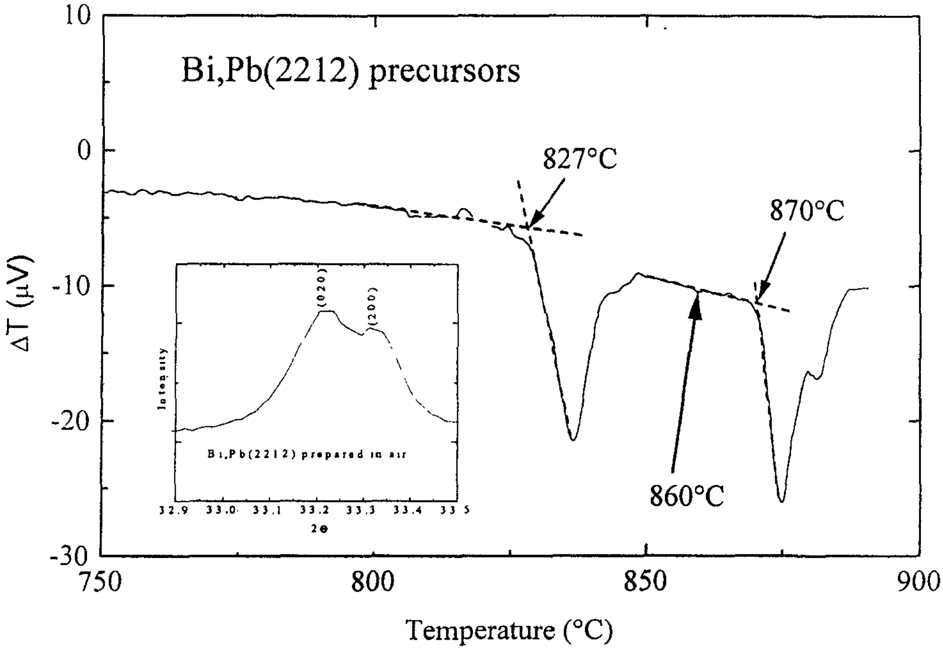

Fig. 6 DTA measurement of a mixture of oxides and carbonates of nominal composition Bi,Pb(2212). The stability range of the Bi,Pb(2212) is situated between 850 and 870°C

sized under argon around 740°C [17, 18]. With a few DTA runs, we have shown that it was possible to prepare this phase in air, but at higher temperatures [19]. Figure 6 shows the DTA measurement for Bi,Pb(2212) precursors under flowing air. There are 2 endothermic peaks respectively at 827 and 870°C. As was determined when forming Bi,Pb(2212) under argon, the ideal synthesis conditions are at temperatures located between the two endothermic peaks so that partial melting has already occurred but the total decomposition has not yet taken place. A temperature of 860°C allows to produce phase pure Bi,Pb(2212) as can be seen in the inset of Fig. 6 where one can see the characteristic separation of the X-ray diffraction peaks of Miller indices (020)(200) indicative of Pb solubility in Bi(2212).

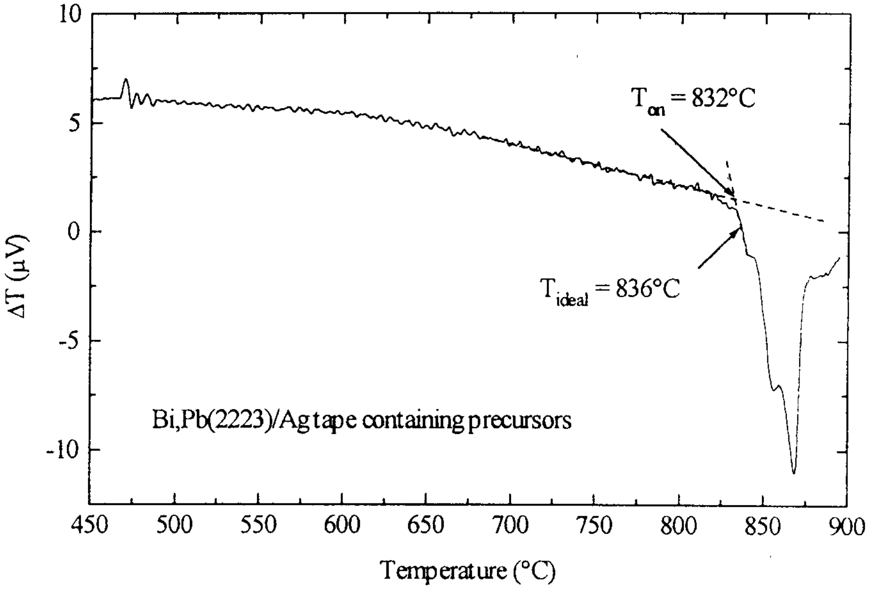

Fig. 7 DTA measurement of a silver sheathed tape containing precursors showing the onset of the first endothermic peak. T_{on} and the ideal annealing temperature T_{ideal} for obtaining high critical current densities

High critical current densities in Bi,Pb(2223) silver sheathed tapes

In our work, we have prepared different precursor powders for the fabrication of silver sheathed Bi,Pb(2223) tapes. However, the preparation parameters are very sensitive to a vast number of parameters including the precursor mixture, composition, deformation process, grain size and homogeneity of the precursors. In order to compare our different samples, we have undertaken a systematic study by DTA/TG of the tapes and have devised a method of determining the optimal annealing temperature to obtain high critical current densities. It has to be pointed out that for the preparation of Bi,Pb(2223)/Ag tapes, we first introduce precursor powders into an Ag tube, which is then deformed and annealed for the transformation to Bi,Pb(2223). Figure 7 shows the DTA measurement of an Ag tape containing precursors. By a systematic study of numerous tapes, the ideal temperature for obtaining high critical current densities has been determined as follows:

$$T_{\text{high jc}} = T_{\text{on}} + (3 \text{ to } 4)^{\circ}\text{C}$$

where T_{on} is the onset temperature of the first endothermic peak observed in the DTA measurement. Indeed, tapes annealed at this temperature have critical current densities at 77 K and OT around 30 kA cm^{-2} [6]. However, tapes annealed at a temperature just 5°C above or below this $T_{\text{high jc}}$, have critical current densities at least a factor 4 lower, this factor increasing as the temperature difference increases. This novel technique is now routinely used for Bi,Pb(2223)/Ag tape preparation.

This temperature is situated just after the beginning of the appearance of a liquid enhancing the transformation to Bi,Pb(2223) and ensuring good grain connectivity. It is also before the total decomposition of the precursor powder preserving some of the precursor.

Assmann *et al.* [12] and Aota *et al.* [20] have also used a similar technique with DTA to form Bi,Pb(2223). Their conditions were however much wider, with an interval of possible temperatures of about 10°C. The difference is that these authors were only preparing bulk material without the additional constraint of having to obtain high critical current densities after the heat treatment. Indeed, in order to obtain these high densities, it is not sufficient to have Bi,Pb(2223) inside the tape, but there has to be an excellent grain connectivity to be able to pass high currents. As we have shown, this is only obtained in a very restricted interval of annealing temperatures after some partial melting has started.

Conclusion

We have shown that DTA/TG can be very useful for studying complex systems like the high temperature superconductors, notably in the Bi–Pb–Sr–Ca–Cu–O system. Characterization of the different phases present including the superconducting and the secondary phases has made it possible to identify some endothermic peaks on DTA curves of different phase mixtures and observe the presence of an intermediate phase Bi,Pb(2212) during the formation of Bi,Pb(2223). It has also helped confirm some phase diagrams in the literature like CaO–PbO and CaO–CuO. DTA has proved essential for the synthesis of new high temperature superconductors like the Pb-containing Bi,Pb(2212). It has been possible by finding the best preparation temperatures which are located before the main DTA peak of measurements of the precursor mixture. This technique has also been used for the preparation of Bi,Pb(2223) silver sheathed tapes. The optimal annealing temperature can be determined by DTA measurements. Critical current densities of about 30 kA cm^{-2} at 77 K and OT have been obtained.

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