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# DTA/TG STUDY OF THE FORMATION OF THE $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$ SUPERCONDUCTOR

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## Abstract

In order to get insight in some of the yet unanswered questions about the formation process of the $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$ superconducting compound, coupled DTA-TG measurements have been performed in parallel with other techniques such as X-ray diffraction, Scanning Electron Microscopy and Energy Dispersive X-ray Microanalysis. The path leading to the formation of the $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$ compound, starting from coprecipitated oxalates powders was studied. The activation energy of some of the involved transformation processes were determined. Relationships between the differences induced in the DTA traces by various sample nominal compositions and the intergranular magnetic properties of the superconductor will be discussed.

**Keywords:** DTA/TG, superconductors

## Introduction

Among the numerous layered cuprates exhibiting superconducting properties at temperatures above 77 K, the $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$ phase (noted Bi,Pb(2223) in the following) has received most attention in the last years since it appears up to now to be the best suited for the elaboration of superconducting devices operating at liquid nitrogen temperature. Nevertheless, due to the small stability domain of this phase [1] and the Pb losses that can occur during the sintering process at high temperature, it has been proven to be difficult to reproducibly obtain nearly single phase products. A detailed knowledge of the formation process seems to be necessary to improve the performances of this ceramic material. However, the complexity of the system has not yet allowed a complete understanding of this phase formation process.

This report presents some investigations performed on the various stages of the preparation and formation of the Bi,Pb(2223) phase by use of coupled DTA/TG measurements in parallel with other experimental techniques, in particular X-ray powder diffraction.

## Experimental

The starting reagents used in this work consisted of commercially available coprecipitated oxalates (Furu-Uchi, Japan). Unless otherwise stated, a nominal molar

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cation ratio of Bi:Pb:Sr:Ca:Cu=1.72:0.34:1.83:1.97:3.13 was used. The precursor powders for the synthesis of the Bi,Pb(2223) phase were prepared by dehydration and decomposition of the oxalates at 500°C in air. After a precalcination of 5 h at 750°C the resulting powders were pressed into pellets under a pressure of 40 MPa and calcined at about 820°C for 48 h with one intermediate grinding and repelletising. At this stage, the powders consisted of a mixture of the $(Bi,Pb)_2Sr_2CaCu_2O_{8+\delta}$ (hereafter Bi,Pb(2212)), $Ca_2PbO_4$, CuO and $(Ca,Sr)_2CuO_3$ phases, with a mean grain size of 3–5 μm after hand-grinding in an agate mortar. For the DTA/TG measurements and the synthesis of the Bi,Pb(2223) phase, the calcined precursor powders thus obtained were pressed into pellets of about 45 mg with 3.6 mm diameter and about 1 mm thickness under a pressure of 1.0 GPa (samples in bulk form). For the tape preparation, some of the precursor powder was introduced in an Ag tube, which was subsequently mechanically deformed by swaging, drawing and rolling to obtain tapes with an overall thickness of 0.1 mm and width of 2.5 mm. The sintering treatments were performed in air. At the end of each treatment, the alumina crucible containing the samples was removed directly in air. No further annealing was performed prior to measurements.

DTA/TG measurements have been performed using a SETARAM TAG 24 thermal analyzer with $Al_2O_3$ as reference in flowing synthetic air ($O_2$ 21%, $N_2$ 79%) or argon, under atmospheric pressure. The 8 mm deep, cylindrical $A1_2O_3$ crucibles had an internal diameter of 4 mm and a wall thickness of about 0.5 mm. The thermocouples (Pt–PtRh 10%) were located under the crucibles, in contact with their bottom walls. The various heating rates used are indicated in the text along with the corresponding sample characteristics.

The room temperature X-ray diffraction patterns of powdered samples were recorded on a Philips Θ–2Θ diffractometer (Ni filtered $CuK_\alpha$ radiation $\lambda=1.54$ Å). For the high-temperature X-ray diffraction, a Huber camera equipped with a heater was used. AC-susceptibility measurements were performed on sintered pellets in a magnetic field of 10 μT rms at a frequency of 81 Hz between 15 and 120 K. The composition of the phases formed in the samples was determined by an energy dispersive X-ray (EDX) analyzer Tracor on polished sections of the pellets.

## Results

Figure 1 shows a TG measurement performed in flowing synthetic air between 30 and 900°C on the starting oxalate mixture with a heating rate of 0.2°C $min^{-1}$. 8.62 mg of powders were placed in the crucible without compaction. After the dehydration process occurring below 200°C, the conversion of the oxalates to oxides or carbonates proceeds stepwise and is complete at about 420°C. A similar measurement performed in a flowing argon atmosphere resulted in a larger weight loss. This is due to the fact that Cu, Bi and Pb oxalates are converted to metals instead of oxides as is the case in air. The DTA curve recorded in air with a heating rate of 2°C $min^{-1}$ exhibits exothermic peaks at the temperatures at which the decomposition of the oxalates occurs (inset in Fig. 1). These peaks are thought to be due to the

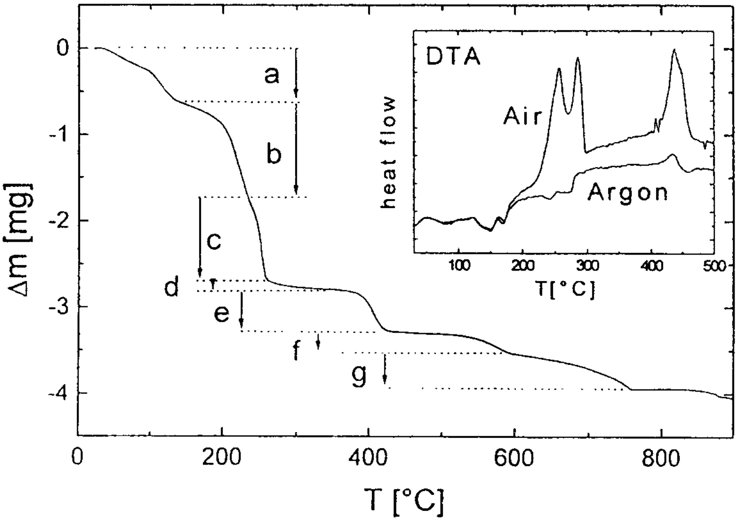

Fig. 1 TG measurement performed on a 8.62 mg sample of coprecipitated oxalates powders with a heating rate of 0.2°C $\text{min}^{-1}$ a: dehydration;
b: $CuC_2O_4+1/2O_2 \rightarrow CuO+2CO_2\uparrow$ c: $Bi_2(C_2O_4)_3+3/2O_2 \rightarrow Bi_2O_3+6CO_2\uparrow$;
d: $PbC_2O_4+1/2O_2 \rightarrow PbO+2CO_2\uparrow$; e: $CaC_2O_4 \rightarrow CaCO_3+CO\uparrow$ and
$SrC_2O_4 \rightarrow SrCO_3+CO\uparrow$; f: $CaCO_3 \rightarrow CaO+CO_2\uparrow$ and
$2CaO+PbO+1/2O_2 \rightarrow Ca_2PbO_4$; g: $SrCO_3 \rightarrow SrO+CO_2\uparrow$
The insert shows DTA measurements performed on powders of the same batch in air and in argon with a heating rate of 2°C $\text{min}^{-1}$

combustion of the CO released during the decomposition. The weight loss corresponding to the conversion of $CaCO_3$ to CaO (f in Fig. 1) is slightly lower than expected for the loss of $CO_2$ from the Ca carbonate.

It was found by high-temperature X-ray diffraction (Fig. 2) that the $Ca_2PbO_4$ compound formed from PbO and CaO in the same temperature range. In $Ca_2PbO_4$, the Pb is in the 4+ oxidation state instead of 2+ as is the case in PbO, thus requiring the gain of one oxygen atom for each Pb atom present in the starting mixture. Actually, the weight loss observed between 420 and 580°C quantitatively corresponds to the superimposition of the conversion of $CaCO_3$ to CaO and the absorption of $O_2$ to form the $Ca_2PbO_4$ phase.

Figure 3 shows the simultaneous DTA and TG measurements performed on the calcined precursor powders in the form of an Ag-sheathed tape with a heating rate of 0.5°C $\text{min}^{-1}$ in flowing air. A first weight loss occurring from room temperature up to about 550°C is due to the release of substances such as $CO_2$ and $H_2O$ that were adsorbed on the sample during the preparation procedure in air and possibly to a release of $O_2$ from the Bi,Pb(2212) present in the sample. A slight weight increase of about 0.073 mg is observed just below 600°C ($\Delta m_1$ in Fig. 3).

It was found by X-ray diffraction [2] that in this temperature region a small amount of a phase described as $Pb_3Sr_{2.5}Bi_{0.5}Ca_2CuO_y$ (or 3321 phase) is formed. This phase being isostructural with $Pb_{2.03}Sr_3Cu_{0.73}O_{7.7}$ [3], contains Pb in the 4+

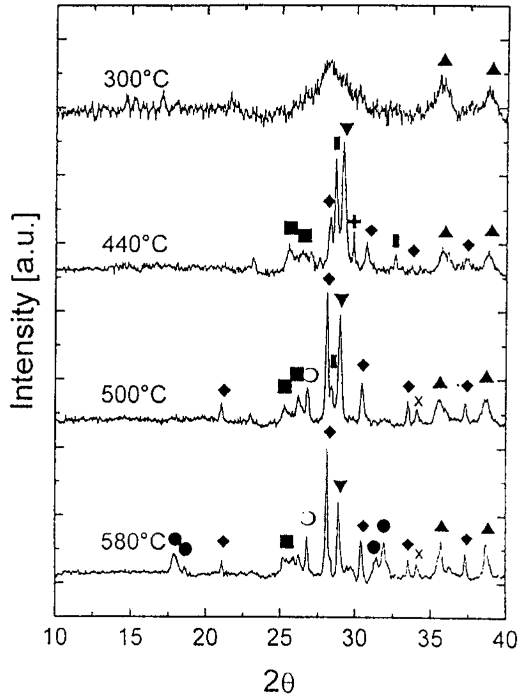

**Fig. 2** High-temperature X-Ray diffraction patterns obtained on the starting reagents after equilibration for 6 h at various temperatures. ▲ CuO, ▮ $Bi_2O_3$, ◆ $Bi_2CuO_4$, ▼ PbO, ✚ $CaCO_3$, o CaO, ■ $SrCO_3$, x SrO and ● $Ca_2PbO_4$

oxidation state. In the Bi,Pb(2212) phase, Pb is on the contrary believed to be in the 2+ oxidation state [4]. Since at the initial stage, Pb was only found by EDX in $Ca_2PbO_4$ and Bi,Pb(2212) it was concluded that Pb is released from the Bi,Pb(2212) phase, either alone or along with some other cations and reacts with the remaining of the matrix to form the 3321 phase, in which process $Pb^{2+}$ is oxidized resulting in a net weight increase of the overall sample. EDX measurements confirmed that small amounts of Pb were contained in the Bi,Pb(2212) phase after the calcination of the precursor powders. Nevertheless, this amount was near the resolution limit of the method and it was not possible to accurately determine the amount of Pb removed from the Bi,Pb(2212) phase during this process. However, the weight increase of 0.073 mg enables an estimation of the quantity of Pb that undergoes the oxidation $Pb^{2+} \rightarrow Pb^{4+}$. This quantity amounts to about 12% of the total Pb content of the initial sample.

A similar effect was found to occur in samples prepared by use of a mixture of intentionally heavily Pb doped Bi,Pb(2212) and alkaline earth cuprates in the form of Ag-sheathed tapes as well as in bulk samples [2, 5].

The endothermic peak (* in Fig.3) is due to a partial melting of the sample [6]. The sharp weight loss occurring during this reaction ($\Delta m_2$ in Fig. 3) is likely to be

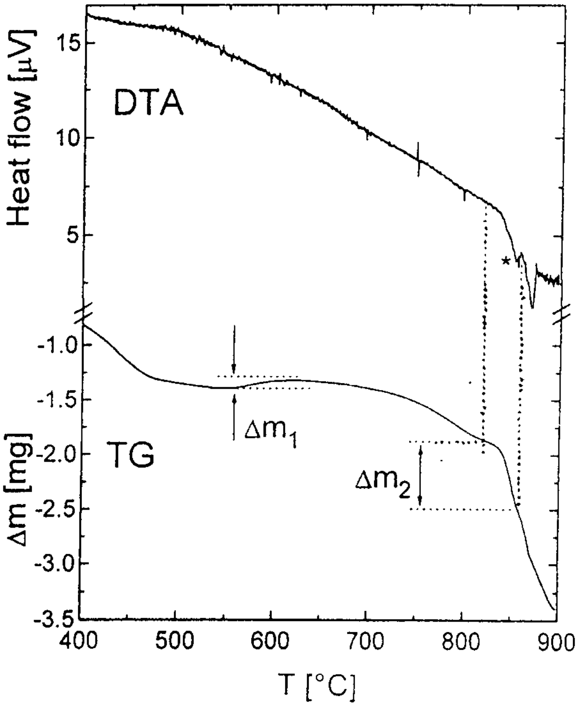

**Fig. 3** Simultaneous DTA/TG measurement performed on an Ag-sheathed tape containing the calcined precursor powders. Total sample mass: 504 mg. Mass of powder: ≈110 mg

related to the disappearance of the $Ca_2PbO_4$ and 3221 phases by reaction with other compounds of the matrix. During this stage, Pb was found by EDX to be again incorporated into the Bi,Pb(2212) phase [7]. Considering that one oxygen atom is released by each Pb atom, the maximum expected weight loss (assuming that all the Pb contained in the nominal composition enters into consideration) is equal to 0.60 mg, in good agreement with the experimentally observed 0.62 mg for $\Delta m_2$.

The activation energy for the partial melting reaction was estimated from DTA measurements performed with various heating rates (1, 2, 4, 6, 8 and 10°C min$^{-1}$) on samples in bulk form prepared as described in the experimental section, in order to avoid a possible influence of Ag. The relation derived by Bansal and Doremus [8] was used:

$$\ln\left(\frac{T^{*2}}{\alpha}\right) = \ln\left(\frac{E_{act}}{R}\right) - \ln(\nu) + \frac{E_{act}}{RT^*}$$

where $T^*$=maximum reaction rate temperature, $\alpha$=heating rate, $R$=gas constant and $\nu$=frequency factor. Since we used a DTA apparatus and not a power compensated DSC calorimeter, $T^*$ did not correspond to the temperature of the maximum deflection of the recorded peak. In DTA measurements, the maximum deflection temperature of a peak corresponds to the maximum rate of heat evolution detected by the differential thermocouples. It does not in general correspond to the maximum rate of reaction [9]. Indeed, using such points for $T^*$ resulted in a non linear dependency of $\ln(T^{*2}/\alpha)$ on $1/T^*$. Instead, we used the temperature corresponding to the maximum of the first derivative of the DTA traces for $T^*$. Although not strictly corresponding to the maximum reaction rate, the temperature found by this method is a reasonable approximation for $T^*$. This temperature approximately coincided with 60% of the maximum intensity of the peak.

Figure 4a shows that in this case there is a linear relationship between $\ln(T^{*2}/\alpha)$ and $1/T^*$ yielding a value of 4000±200 kJ $\text{mol}^{-1}$ for $E_{act}$. The value of $E_{act}$ was also estimated using the temperature corresponding to various relative extents of the development of the peak for $T^*$. $\ln(T^{*2}/\alpha)$ *vs.* $1/T^*$ plots with $T^*$ corresponding to 35 to 85% of the maximum intensity of the endothermic peak systematically yielded $E_{act}$ values comprised between 3600 kJ $\text{mol}^{-1}$ and 4450 kJ $\text{mol}^{-1}$. However, the linearity of the dependency of $\ln(T^{*2}/\alpha)$ on $1/T$ was the best for 60%.

The formation of the Bi,Pb(2223) phase itself can not be recorded during DTA/TG measurements, probably due to its slow formation rate. Therefore, the activation energy for this formation was obtained from an analysis of the XRD patterns recorded on samples heated in air with a heating ramp of 2°C $\text{min}^{-1}$ up to various temperatures and quenched in air after 20 h sintering. The transformed volume fraction of the pellets was estimated by comparison with standard powder mixtures following a method described elsewhere [10]. The time dependence of the transformation was assumed to follow the Avrami relation for isothermal transformations, which was reported to be well suited to describe the process [11]. In this relation, where the transformed volume fraction $V$ of the sample is given by:

$$V = 1 - \exp[-kt^n]$$

where $k$ is the reaction rate and $n$ an exponent dependent on the nature of the transformation, the rate constant $k$ is assumed to follow an Arrhenius type of relation:

$$k = k_0\exp[-E_{act}/RT]]$$

where $k_0$ is a constant, $E_{act}$ is the activation energy and $R$ is the gas constant.

This enables an estimation of $E_{act}$ from a $\ln[-\ln(1-V)]$ *vs.* $1/T$ plot (Fig. 4b). The $E_{act}$ of 870±70 kJ $\text{mol}^{-1}$ found for the formation of the Bi,Pb(2223) phase is significantly lower than that corresponding to the partial melting reaction (4000 kJ $\text{mol}^{-1}$). It must however be emphasized that the activation energy for the formation of the Bi,Pb(2223) phase is sensitive to the details of the experimental procedure [10].

The intensity of the DTA peak due to the partial melting and hence the amount of liquid phase formed in the sample, naturally depends on the nominal composition of the sample. Figure 5 shows the DTA traces obtained in flowing air with a heating rate of 2°C $\text{min}^{-1}$ on calcined precursor powders with 4 different nominal compositions, prepared under the same conditions. The samples consisted in 45 mg pellets of compacted powders. It appears that the compositions that are richer in Cu pres-

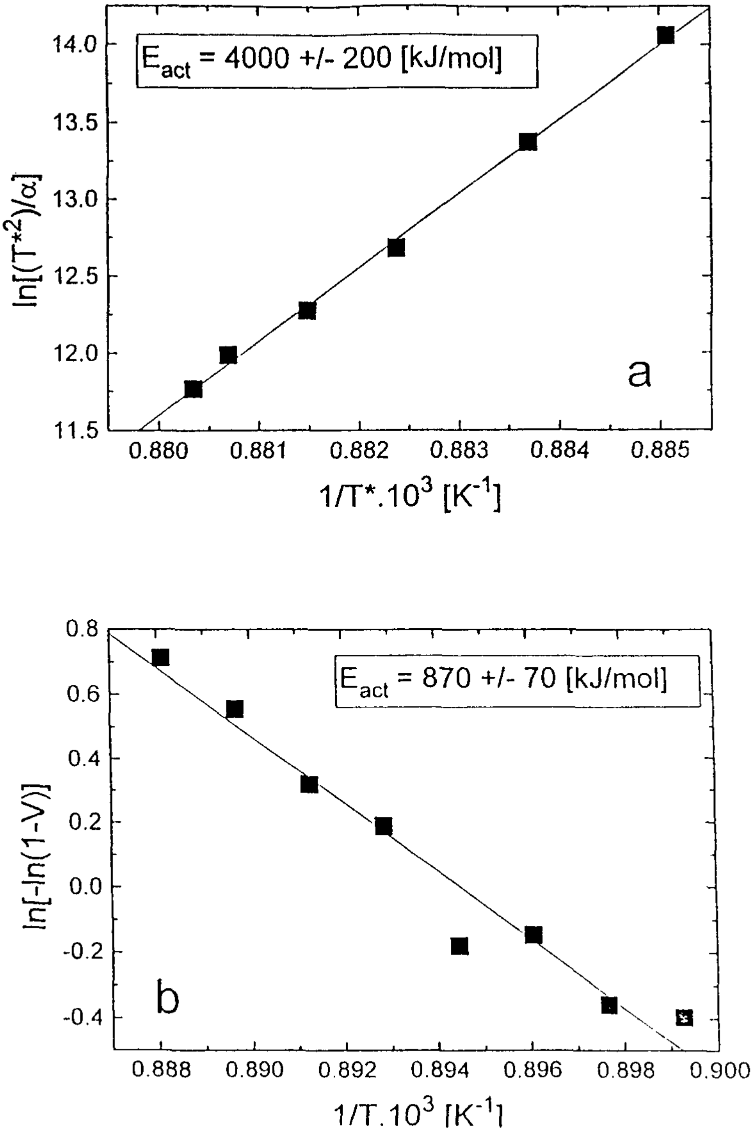

**Fig. 4** (a) $\ln[(T^{*2})/\alpha]$ *vs.* $1/T^*$ plot obtained from DTA measurements performed with various heating rates on calcined precursor powder pellets; (b) $\ln[-\ln(1-V)]$ *vs.* $\ln(t)$ plot obtained from pellets sintered during 20 h at various temperatures. (caption of Fig. 5)

ent the more prominent partial melting peak. This is not surprising since CuO is implied in this reaction [7].

Pellets of those calcined precursor powders have been sintered at 857°C for various lengths of time, resulting in the formation of the Bi,Pb(2223) phase. The

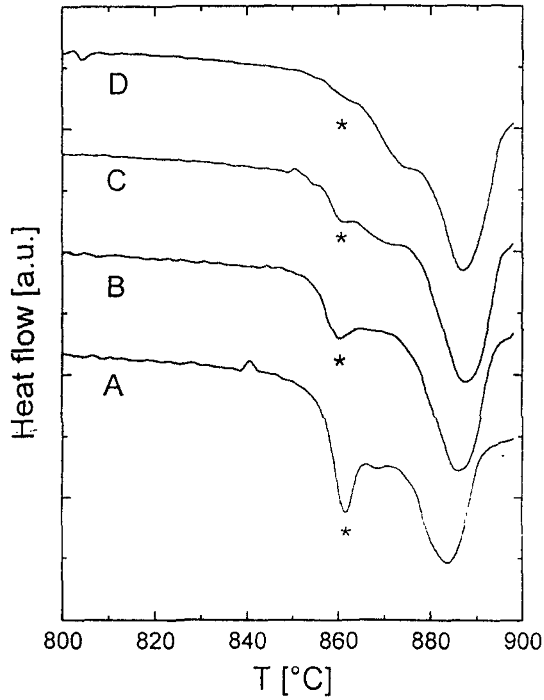

**Fig. 5** DTA measurements performed on calcined precursor powders with various nominal compositions: A: $Bi_{1.72}Pb_{0.34}Sr_{1.83}Ca_{1.97}Cu_{3.13}O_{10+\delta}$, B: $Bi_{1.84}Pb_{0.34}Sr_{1.81}Ca_{2.03}Cu_{3.06}O_{10+\delta}$, C: $Bi_{1.80}Pb_{0.40}Sr_{2.00}Ca_{2.20}Cu_{3.00}O_{10+\delta}$, D: $Bi_{1.80}Pb_{0.33}Sr_{1.93}Ca_{1.93}Cu_{3.00}O_{10+\delta}$ (* indicates the endothermic peak due to the partial melting reaction)

imaginary component ($\chi$") of the ac-magnetic susceptibility of the sintered samples revealed a peak characteristic of the intergranular superconducting transition (inset in Fig. 6). The temperature at which this transition occurs depends on the quality of the grain boundaries, a higher temperature reflecting better coupling properties. In Fig. 6, the evolution of this temperature as a function of time is reported. The progressive increase of the temperature at which the intergranular transition occurs indicates that the Bi,Pb(2223) grains are better connected as the formation of the phase proceeds. A difference is apparent between the 4 investigated compositions in that those which induce the more prominent partial melting peak, present the lowest intergranular superconducting transition temperatures. Assuming that the growth of the Bi,Pb(2223) phase grains proceeds in presence of a liquid phase in which excess Cu is present, it can be expected that Cu is segregated at the grain boundaries. In such a case, a better coupling between the crystallites of the Bi,Pb(2223) phase in the samples in which a lower amount of Cu is implied during the formation of the liquid phase, can be understood.

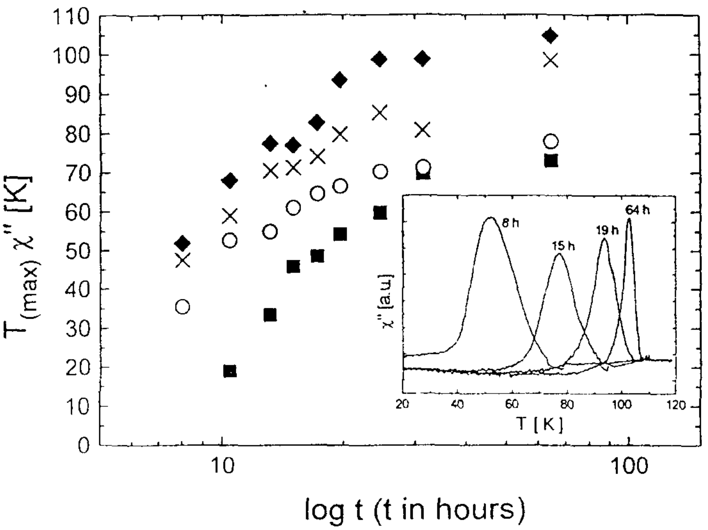

**Fig. 6** Intergranular superconducting transition temperature *vs.* sintering time (*t*) for the nominal compositions: A: $Bi_{1.72}Pb_{0.34}Sr_{1.83}Ca_{1.97}Cu_{3.13}O_{10+\delta}$ (■), B: $Bi_{1.84}Pb_{0.34}Sr_{1.81}Ca_{2.03}Cu_{3.06}O_{10+\delta}$ (○), C: $Bi_{1.80}Pb_{0.40}Sr_{2.00}Ca_{2.20}Cu_{3.00}O_{10+\delta}$ (×), D: $Bi_{1.80}Pb_{0.33}Sr_{1.93}Ca_{1.93}Cu_{3.00}O_{10+\delta}$ (◆). The insert shows the imaginary component ($\chi''$) of some of the ac-susceptibility measurements performed on pellets with composition D after sintering at 857°C for various durations indicated in hours above the corresponding curves

## Conclusions

It has been shown that the Bi, Pb, Sr, Ca and Cu oxalate mixture decomposes below 420°C resulting in the formation of $Bi_2O_3$, PbO, $SrCO_3$, $CaCO_3$ and CuO, whereas the $Ca_2PbO_4$ compound forms from PbO, CaO and oxygen at about 550°C.

After calcination at 820°C, the Bi,Pb(2212) phase formed in the precursor powders contains a small amount of Pb. This Pb tends to be released out of this phase around 600°C during a further heating, resulting in the formation of the 3321 phase.

During the partial melting reaction occuring above 820°C, a weight loss corresponding to a loss of oxygen during the reduction of $Pb^{4+}$ to $Pb^{2+}$ is observed. The activation energy of the partial melting reaction was found to be 4000±200 kJ $mol^{-1}$ whereas that corresponding to the formation of the Bi,Pb(2223) phase is of 870± 70 kJ $mol^{-1}$.

The temperature of the intergranular superconducting transition measured by ac-susceptibility on sintered samples with various nominal compositions was found to depend on the intensity of the partial melting peak recorded by DTA.

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