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THERMAL INVESTIGATIONS OF REACTIVE POWDER MIXTURES AS PRECURSORS FOR MELT-PROCESSING OF $YBa_2Cu_3O_{7-x}$

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Abstract

DTA and XRD measurements were carried out with reactive precursors taken from the $YO_{1.5}$–BaO–CuO system in order to investigate mechanisms of $YBa_2Cu_3O_{7-X}$ formation. The reactions taking place depend strongly on phase composition, phase purity, powder size and heating rate. Among the examined reactive precursors a mixture of $7Y_2O_3+22BaCuO_2+10CuO$ turned out as the most suited for melt-processing.

Keywords: DTA, superconductor

Introduction

Melt processing is widely accepted to yield the best superconducting properties in bulk YBCO. All melt processes proposed by now are represented by the following scheme:

$$\text{123-precursors} + \text{additions} \xrightarrow{1} 211 + \text{liquid} \xrightarrow{2} 123 + \text{other phases}$$

(123-phase = YBCO = $YBa_2Cu_3O_{7-x}$, 211-phase = Y_2BaCuO_5).

In the first step, a preformed powder mixture is heated to 1000–1100°C, forming the properitectic phase 211 and a partial liquid, in the second step the configuration is cooled down in a temperature gradient, enforcing peritectic growth of 123 grains and eventually the formation of other phases.

Step 2 is both complicated and time consuming; thus many studies have been carried out about the mechanism [1–3] and technological aspects [4, 5] of melt-texturing. Due to incomplete peritectic reaction some of the 211-particles are usually trapped within the 123-phase. With respect to good magnetic properties of melt-textured YBCO (improved pinning) it is highly desirable to achieve a homogeneous distribution of these entrapped 211-particles inside the superconducting 123-phase as well as to decrease their mean size. Therefore much effort has been made in reducing the size of the 211-particles. Platinum doping, for example, was successfully used for this purpose [6]. An easier way to achieve fine 211-particles in the melt, even without doping, is to make use of reactive precursor materials [7]. It has been

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shown for example, that the use of a reactive mixture of Y_2O_3, $BaCuO_2$ and CuO yields a very homogeneous distribution of 211-inclusions exhibiting a mean size of µm without any dopants, Fig 1. Alternatively mixtures containing 211 instead of Y_2O_3 have been investigated [8, 9].

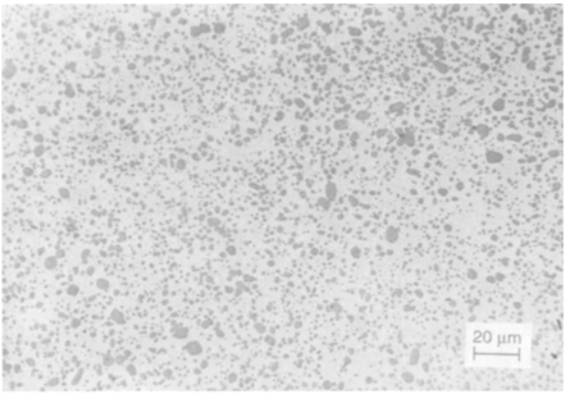

Fig. 1 Small-sized (mean Ø ≈ 1µm) 211-inclusions in a matrix of 123, fabricated from mixture (I) (1 cm ≅ 20 µm)

The present work concerns mainly step 1 and the possibilities to determine size and distribution of 211 particles ab initio. Because the mechanism of 211-formation is still under discussion, the reactions taking place in reactive precursor mixtures during the heating step were investigated. Furthermore the influence of phase composition, the ratio Y_2O_3:$BaCuO_2$:CuO, grain size, phase impurities, heating rate and precedent reactions at lower temperatures on these reactions were examined.

The critical current density of the processed samples depends on composition, the size of the precursors and the thermal processing (sintering [10–12], high-pressure sintering [13, 14] and texturation [9, 15–17]) and has values of 10^2–10^4 A/cm^2.

Experimental

Pure phases of $BaCuO_2$, $YBa_2Cu_3O_{7-x}$, Y_2BaCuO_5 and $Y_2Cu_2O_5$ were prepared via solid state reactions, using either stoichiometrical mixtures of $BaCO_3$, CuO and Y_2O_3 or coprecipitated oxalates. Calcination was carried out twice with an intermediate grinding step. After the second step the samples were splat quenched. A lower calcination temperature was chosen for the coprecipitated powders due to their lower particle size, Table 1.

Powder mixtures, differing either in their composition or in their mean particle size, were prepared from above pure phases. Due to the simplicity in preparation mixtures containing the components Y_2O_3, $BaCuO_2$ and CuO were analyzed more closely. They were prepared in three different compositions: The ratio Y_2O_3:$BaCuO_2$:CuO (200:011:001) like 1:4:2, yielding an overall stoichiometry of "123", and two mixtures with the ratios 7:22:10 (I) and 9:24:10 (II). Mixtures (I) and (II) were chosen with respect to manufacturing purposes.

Table 1 Sintering temperatures and estimated grain sizes of cuprates

Substance	"Dry" precursor	Grain size/μm	"Wet" precursor	Grain size/μm
$BaCuO_2$	860 and 915°C	30–60	750 and 860°C	1–3
$YBa_2Cu_3O_{7-x}$	850 and 950°C	45–100	800 and 900°C	1–5
Y_2BaCuO_5	900 and 1000°C	52–125	850 and 900°C	3–10
$Y_2Cu_2O_5$	900 and 1000°C	45–125	850 and 950°C	5–10

These mixtures were analyzed with a Netzsch DTA/TG at a heating rate of 10 K min^{-1}. For the measurements an amount of 100 mg of each precursor mixture has been used. Three separate calibrations of the apparatus in reference to the melting point of gold delivered values of 1065.3, 1064.8 and 1065°C (true value: 1064.2°C). Repetition of the experiments led to a fluctuation in temperature of about 4 K. The accuracy was therefore estimated with ±2 K. Additional XRD measurements (Stoe, CoK_α, radiation) were employed to determine the phases having formed during heat treatment.

Results and discussion

Thermal characteristics of the reactive powder mixtures

In a first step precursors varying in their phase composition were examined. Figure 2 shows the DTA plots of three reactive powder mixtures of the overall stoichiometry "123" (202+011 [a], 211+011+001 [b], 200+011+001 [c]) compared to 123-phase with 200-additions [d] and pure-phased 123 [e].

The mixtures show thermal effects at onset-temperatures ranging from 916 to 931°C. These effects correspond to reactions between the four phases 211, 202, 011 and 001. In order to determine the reactions taking place in the more complicated systems, which consist of three or more phases, DTA experiments of more simple phase compositions, namely 011+001, 202+011, 211+001 and 211+202+001, were carried out in a second series, Fig. 3.

The reaction 011+001, Fig. 3a, shows an endothermal peak at 915°C which results from a liquid phase formation between the two components, 011+001→liquid [18]. The base-line shift of the curve towards exothermal values indicates the formation of a large amount of liquid. This results from the higher heat conductivity of the liquid, which accelerates the heating of the sample relative to the reference sample. The increase of the curve at higher temperatures might be caused by the reduction of $Cu(II)^{2+}$ to $Cu(I)^{+}$, starting at 1030°C.

Liquid phase formation also occurs between 202 and 011 (Fig. 3b) at 925°C. The corresponding reaction is 202+011→123+211+liquid. A further increase of the temperature causes decomposition of 123 into 211 and liquid, indicated by the second peak, and subsequent reduction of the copperions in the partial liquid, indicated by the increase of the curve.

In the system Y_2BaCuO_5–CuO the two components react to 202+liquid at 954°C. Then, at above 1040°C, the previously formed 202 reacts with residual 211

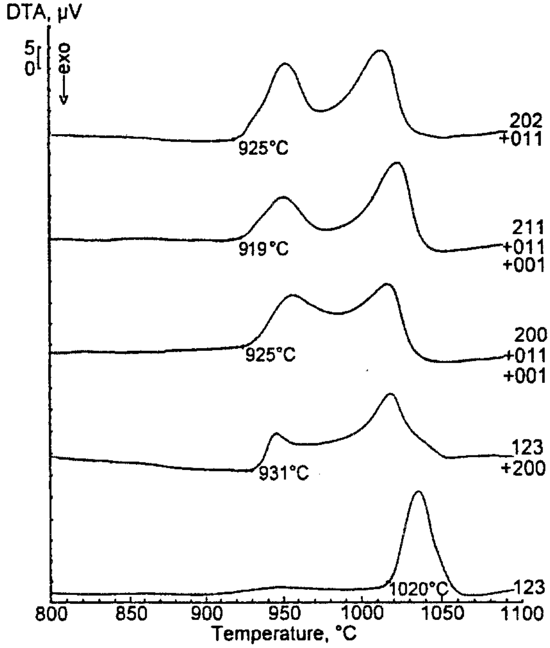

Fig. 2 DTA-curves of three mixtures with an overall stoichiometry 123 (a,b,c), 123 with 200 additions (d) and pure 123 (e)

to 200+liquid, Fig. 3c. The second peak seems to be caused by two overlapping peaks. In order to separate these peaks the experiment was repeated with additional 202 in the phase composition, Fig. 3d. The first reaction 211+001→202+liquid is identical to the previous one with the only difference, that less 211 is consumed due to the presence of 202. The second peak becomes much sharper, it results again from the reaction 202+211+liquid→200+liquid at 1045°C. Now there is still enough residual 211 left for the third reaction to take place, which necessarily has to be 200+211+liquid→200+liquid and starts at about 1050°C. These informations are helpful to determine peaks in the other DTA curves.

In the reaction 211+011+001, Fig. 2b, the first peak at 919°C is caused by eutectic melting of $BaCuO_2$ and CuO. Using 200 as a starting component, Fig. 2c, a solid state reaction of 200 with 001 to 202 at lower temperatures is preferred. This reaction consumes most of the 001-phase, leaving none for the 011+001 liquid formation. Thus the first peak is caused by the 202 decomposition at 925°C, like in Fig. 2a. In the 123–200 system, Fig. 2d, the situation is more complicated. The slight decrease of the base line up to 930°C indicates an exothermal reaction taking place during heating, in which 001 forms via solid-state reaction. The most likely explanation for the peak at 931°C is the melting of 123 in the presence of the 001-phase [19]. Phase pure 123 shows only one endothermal reaction at 1020°C (Fig. 2e) due to peritectic melting.

Concerning the mixtures, it has been shown by means of radiography [20, 21], that 123 formation takes place during heating. Thus the second peak in Fig. 2a–2d

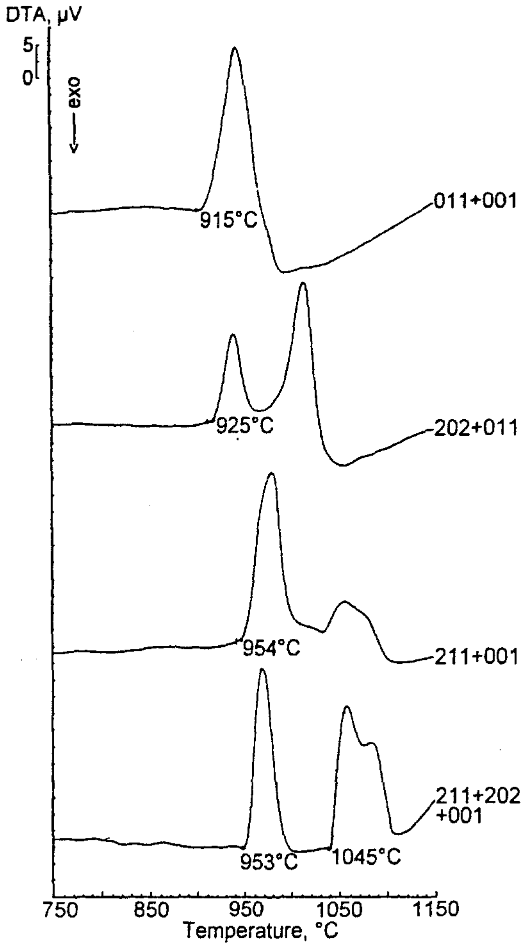

Fig. 3 DTA-curves of binary mixtures 011+001, 202+011, 211+001, 211+202+011

Table 2 Reactions determined by DTA measurements

Reaction	Temperature/°C	Figures
011+001 → liquid	916	3a
202+011 → 123+211+liquid	925	3b
211+001 → 202+liquid	954	3c
123+211+liquid → 211+liquid	1020	3b
202+211+liquid →200+liquid	1045	3c, 3d
200+211+liquid → 200+liquid	>1050	3d

can be identified with the peritectic melting of 123. Due to the presence of impurities Fig. 2a–2c or a shifted overall stoichiometry, (Fig. 2d) the peak onset-temperature is decreased in the mixtures.

In Table 2 the characterized reactions and their corresponding temperatures are listed. Nevertheless these temperatures are a result of dynamical solid-state reactions. They are dependent on the reactive behaviour of the precursors (availability of reaction partners with respect to concentration and grain size) and macroscopical parameters (heating rate, powder density, gas atmosphere, etc.). Also the purity, or better "chemical biography" of the components, especially the 011-phase, has a strong influence on the reactions taking place.

Influence of residual BaCO$_3$

A crucial aspect in melt-processing of YBCO is the presence of residual carbon in the precursor mixtures. Especially when preparing the 011-phase, carbon easily

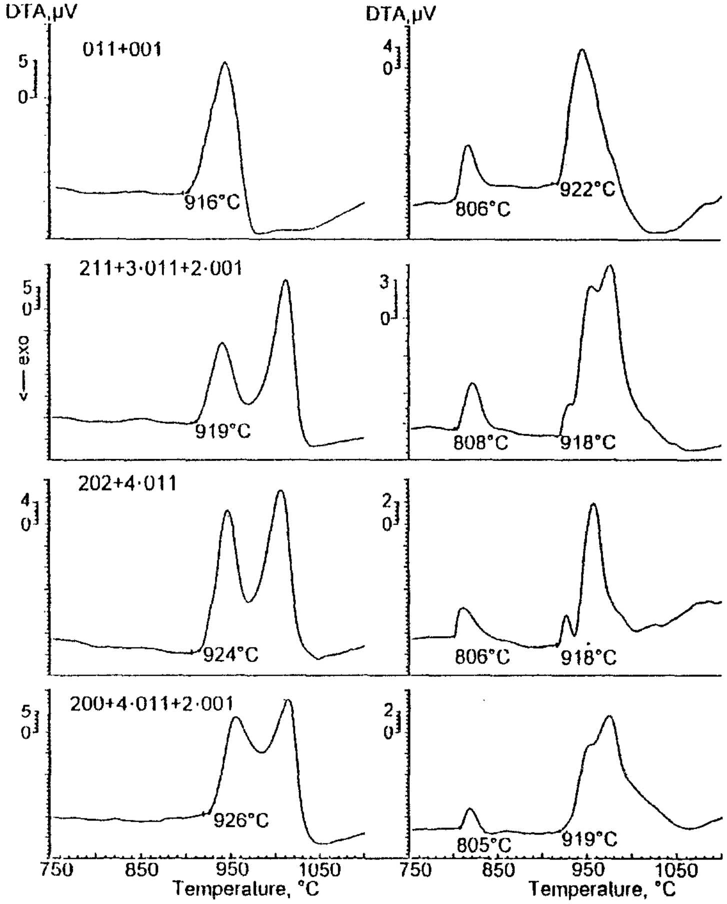

Fig. 4 Influence of BaCO$_3$ impurities on the DTA-curves of mixtures 011+001, 211+3·011+2·001, 202+4·011, 200+4·011+2·001

gets into the samples as barium is highly susceptible for the CO_2 in the processing atmosphere, forming $BaCO_3$. DTA measurements are a sensitive method to detect even small amounts of residual $BaCO_3$, which fail to be detected by means of XRD. The phase transformation $\gamma\text{-}BaCO_3 \rightarrow \beta\text{-}BaCO_3$, taking place at about 810°C reveals a characteristic endothermal peak for carbon contents exceeding 1%. Lower carbon contents can only be detected coulometrically [20, 21].

Figure 4 shows DTA plots of different precursor mixtures without (Fig. 4a) and with $BaCO_3$ additions (Fig. 4b). It is obvious, that samples with $BaCO_3$ impurities have completely different DTA curves. The 123 melting peak is missing, which means that no or only little 123 phase was formed. With an overall stoichiometry of Y:Ba:Cu=1:2:3, the precursor lacks the barium being bound in $BaCO_3$, making the occurrence of secondary phases inevitable and inpredictable [23]. Carbon has also a certain solubility in the partial liquid and biasses the superconducting properties of the sintered samples.

Nevertheless, $BaCO_3$ seems to disappear almost completely in melt-processed samples, since CO_2 evaporates. In this case the high CO_2 content in the processing atmosphere has a bad influence by increasing the sample-porosity. In the cooling step $BaCO_3$ precipitates in the samples [18]. It is even occasionally found on the surface of massive YBCO-samples.

Variation of powder stoichiometry

In next step it was investigated, if a change in the stoichiometric composition of the precursor materials, could be utilized to improve YBCO melt-processes. The measurements in Fig. 5 reveal the influence of surpluses of Y_2O_3 resp. CuO on the reactions taking place during heating. The DTA curves for mixtures of the same phases (200, 011 and 001) with different overall stoichiometry, i.e. 1:1:1 ("$Y_2BaCu_2O_x$", 5a); 1:2:2 ("$Y_2Ba_2Cu_4O_x$", 5b); 1:4:2 ("$YBa_2Cu_3O_x$", 5c) and 1:2:1 "$Y_2Ba_2Cu_3O_x$", 5d). They differ significantly, as the phase composition is eventually changed by solid state reactions at lower temperatures. The first reaction taking place in the system under consideration is 200 + 001→202. The amount of constituting 202 depends strongly on the availability of 001-phase. A qualitative statement about this amount can be derived from the relative height of the corresponding decomposition peak, which reveals the intensity of the reaction. The phases subsequently react, following different univariant reactions. The first peak in all curves is mainly caused by the reaction: 202+011→123+211+liquid, taking place at 925°C. In mixtures 5a and 5d the peak onset temperature is slightly lower (919°C) – probably in these curves the peaks overlap with the peaks of the reaction 011+001→liquid. The reason for that might be the lower amount of 001 in the precursors 5a and 5d, which obstructs the solid state reaction forming 202.

In Fig. 5a and 5b a second peak at 954°C appears, which is caused by the decomposition of 211 in the presence of 001 (211+001→202+liquid). This reaction is preferred in 5b due to a high amount of residual Cu in this mixture. The third peak corresponds to the reaction 202+211+liquid→200+liquid. In Fig. 5b no 123-phase is formed, whereas in 5a the increase of the curve prior to the last peak might reveal the melting of a small amount of 123.

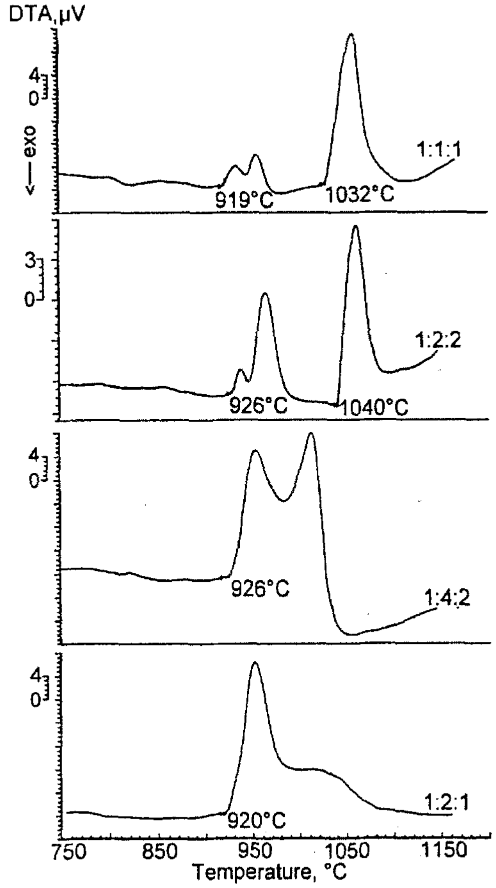

Fig. 5 DTA-curves of mixtures of 200, 011 and 001 with different overall stoichiometries

Figure 5c shows the DTA of the standard precursor mixture with 123-stoichiometry: first of all 200 reacts with 001 to 202 via solid state reaction, followed by the univariant reaction 202+011→123+211+liquid at 926°C. The 211 decomposition peak at 954°C, that occurred in Fig. 5a and 5b seems to be missing, but it is more likely that it is overlapped by the relaxation of the first peak. At about 980°C 123 melts in the presence of secondary phases. In Fig. 5d less 123 is produced, as the lack of 011 in the precursor shifts the equilibrium of the reaction 202+011→123+211+liquid towards 211.

Admixtures of 200-phase to 123-precursor powders for example lower the processing temperature, which results in reduced interaction between sample and crucible. A part of the yttria does not react to 123-phase and remains disperged as 211-inclusion in the 123-matrix (Fig. 1). Sometimes even pure Y_2O_3 inclusions remain in a 211-grain (Fig. 6). Unfortunately an yttria surplus supports the formation of 211-, 202- and 011-phase.

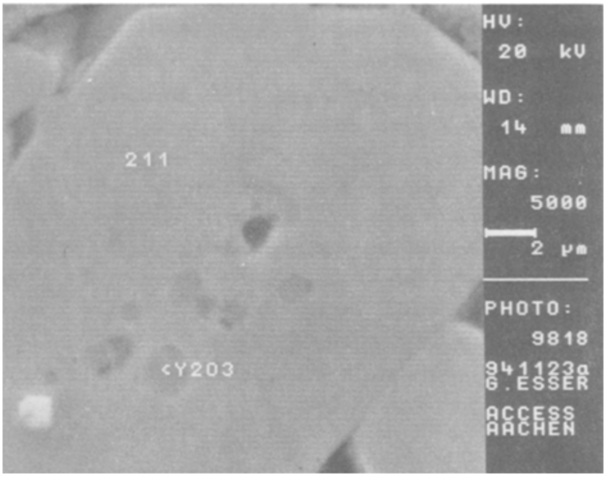

Fig. 6 SEM-micrograph of residual Y_2O_3 in a Y_2BaCuO_5 crystal (1 cm≅2 μm)

A surplus of CuO, remaining in the 123-matrix as unreacted, crystalline inclusions [24], increases the mechanical strength and the density of the superconductor [14]. The ratio between 011-phase and 001-phase is decisive for the amount of formed liquid phase. Reactive mixtures with a surplus of CuO can be sintered at lower temperatures.

Influence of the powder particle size

In order to investigate the influence of a different starting powder size on the reaction mechanism, DTA experiments were carried out with powders of identical stoichiometry and phase composition, but varied particle size, Fig. 7. Three different powders, created from 200, 011 and 001 were analyzed: the composition 1:4:2, 7:22:10 (I) and 9:24:10 (II). Mixtures (I) and (II) have a stoichiometrical surplus of "211" compared to "123", which is intended to remain as small 211-inclusions inside the 123-matrix after processing. These 211-inclusions serve as pinning centers and thus improve the magnetic properties of the superconductor [1, 3]. The stoichiometrical ratio between 123 and 211 figures out to be 5:1 for mixture (I) and 5:2 for mixture (II).

As shown in Fig. 7a, lowering the mean particle size from 125 μm down to 90 μm leads to a sharper 202-decomposition peak. This is mainly due to the reduction of the mean distance between neighbouring particles, which supports the diffusion controlled solid state reactions. Decreasing the particle size to 32 μm leads to no significant change in the DTA-curve, which means that 202-formation is almost complete under these conditions for 90 μm-sized precursors. It is likely that – depending on the heating rate – there is a boundary value in particle size, below which a further reduction has no effect on the reactivity. For the stoichiometrical mixture (1:4:2) this value should be somewhere near 90 μm. Concerning mixtures (I) and (II), neither the different grain sizes, situated far below 90 μm, nor the method of production seem to be of importance.

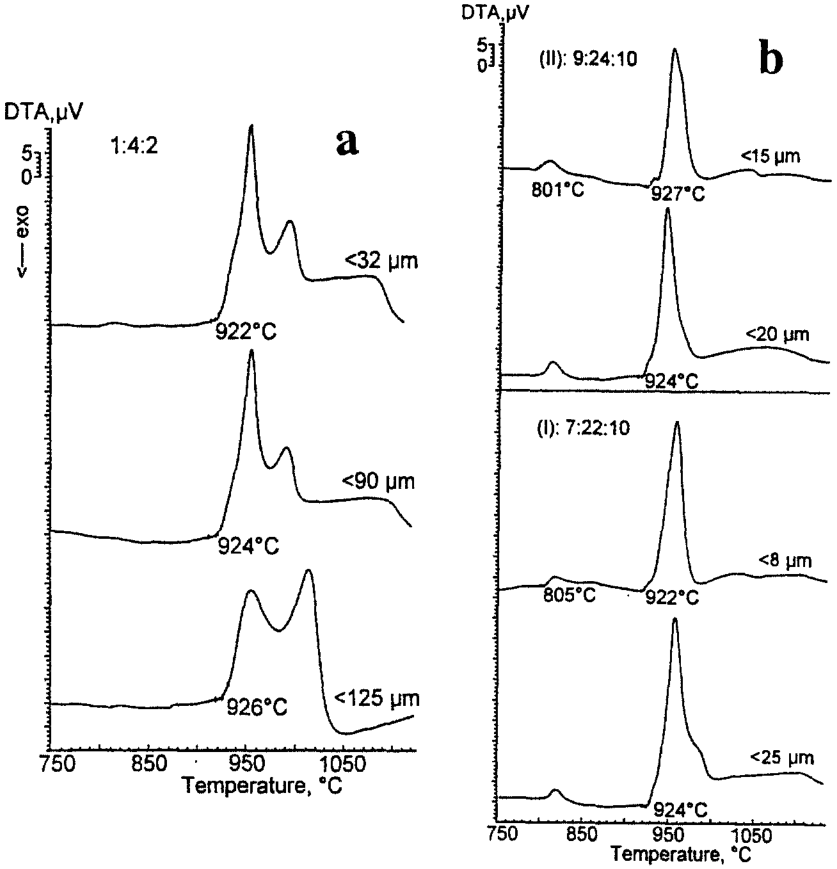

Fig. 7 Influence of the particle size on the DTA-curves of the reactive mixtures: a) 200+4·011+2·001, b) (I) and (II)

As described above, mixtures (I) and (II) were prepared in two different ways, yielding mean sizes of 8 and 25 μm for mixture (I) and 15 and 20 μm for mixture (II). The DTA-curves of these mixtures, Fig. 7 do not differ significantly, so with respect to powder sizes a further reduction has no influence on the reactions taking place.

The grain size is also a technological problem: Powder with grains size smaller than 25 μm can be compacted higher densities if surface of the grains is coarse. For pressing purposes a grain size of about 10 μm is desirable.

Influence of the heating rate

Figure 8 shows DTA measurements of mixtures (I) and (II) conducted at different heating rates. In both mixtures the 123 melting peak can only be observed at lower heating rates (0.5 and 2.5 K min^{-1}). At higher heating rates this peak disappears, which means, that 123 phase formation in these mixtures can be suppressed by sufficiently high heating rates. The reason for that is, that there is not enough time for 123-phase to form via solid state reaction before temperatures exceed the

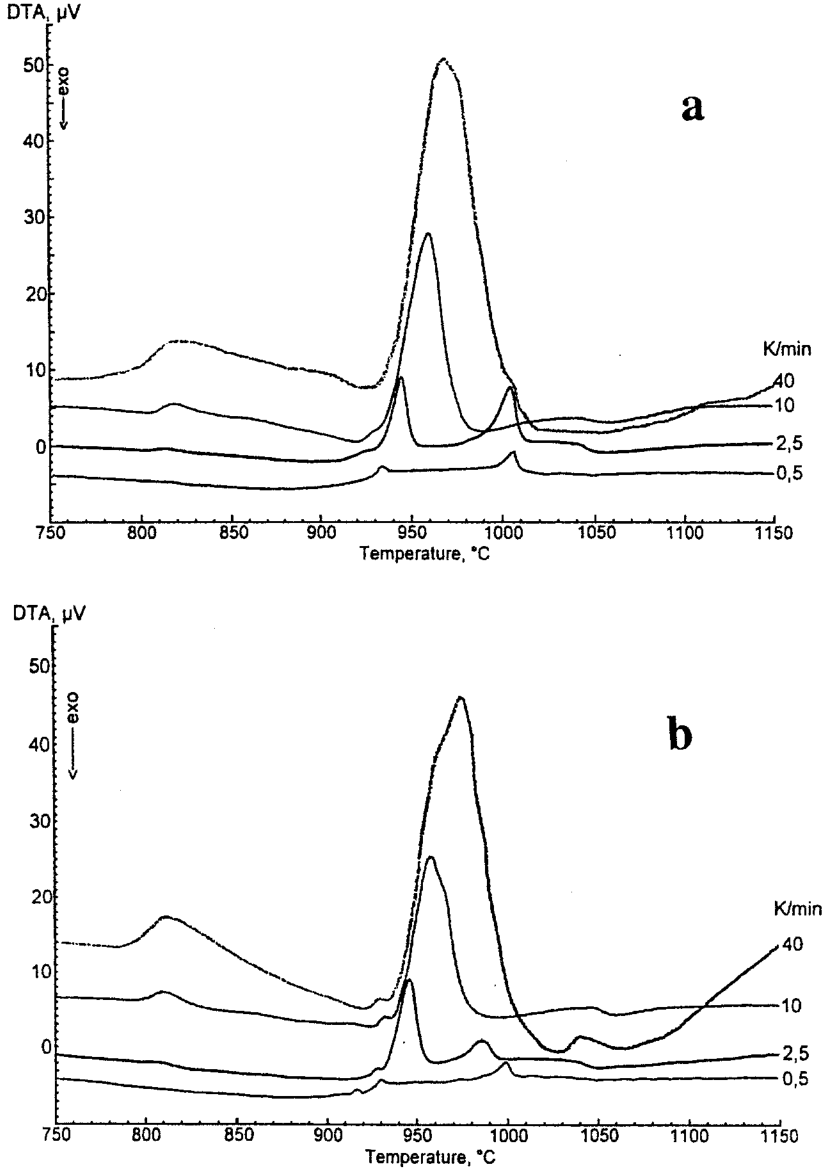

Fig. 8 Influence of the heating rate on the DTA-curves of the reactive mixtures, a: (I), b: (II)

lower heating rates (0.5 and 2.5 K min^{-1}). At higher heating rates this peak disappears, which means, that 123 phase formation in these mixtures can be suppressed by sufficiently high heating rates. The reason for that is, that there is not enough time for 123-phase to form via solid state reaction before temperatures exceed the peritectic melting temperature of 1020°C, above which 211+liquid is stable. The prevention of 123-formation could be beneficial for melt-processing:

It was observed that 211 particles, which arise after peritectic melting of the 123 phase, tend to be larger than those originating from the solid state reaction. Besides the peritectically grown 211 are more needle shaped. The reason for the different behaviour might be, that 211 particles, which originate from the reaction 123→211+liquid at above 1020°C are lowly undercooled with respect to their own melting temperature. Therefore the 211 nucleation rate is very low, which yields fewer and larger 211 grains after processing. In Fig. 9 the mean sizes of 211-inclusions at different processing temperatures are plotted against the processing time. The peritectically grown 211 are notably larger. With no 123-phase having formed via solid state reaction there are no peritectically grown 211-crystals in the sample after processing.

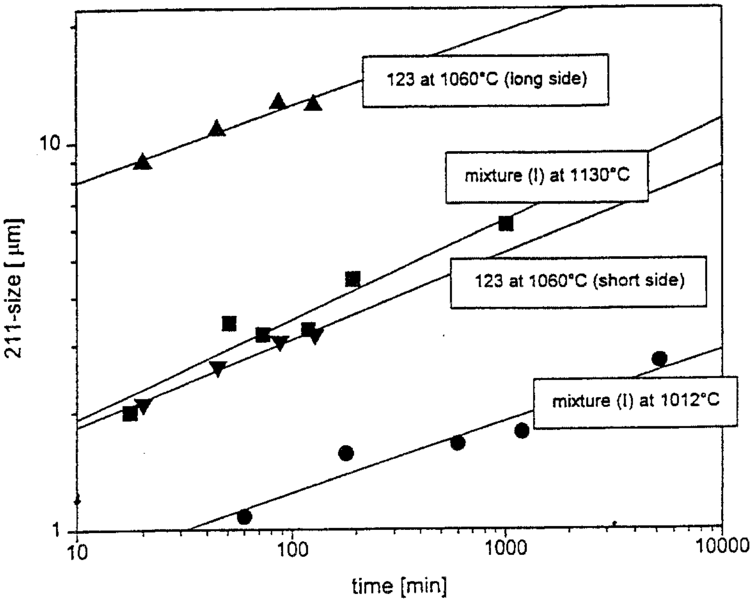

Fig. 9 Mean size of 211 *vs.* time for different processing temperatures

Influence of a preceding thermal treatment

In order to investigate the mechanism of 123-formation in mixtures (I) and (II) more closely, DTA and XRD investigations have been carried out on samples that were previously sintered at different temperatures. Figure 10 shows the DTA plots for samples pre-treated at 850, 900 and 950°C compared to the untreated samples; Figure 11 shows the corresponding XRD plots.

The DTA curves reveal the existence of different amounts of secondary phases, depending on the temperature of pretreatment.

For mixture (I) the amount of secondary phase decreases for samples, that were pretreated at higher temperatures. On the one hand this can be derived from the shift of the 123-melting peak towards higher temperatures, which is the closer to the periteccreases. In the pre-treated samples of mixture (II) this peak increases, which means that more secondary phase is formed at higher temperatures.

Instead of the desired phase composition 123+211, which as well as the pure 123-phase shows no DTA effects below 1000°C [20], the XRD curves reveal the existence of unwelcome 011-phase in almost all mixtures. Only in mixture (I) treated at 950°C there is no 011 phase.

Comparing the intensities of the strong lines of the 123 and 211-phase (Fig. 12) reveals the influence of the temperature of pretreatment on the built up of the phases. In mixture (I) the intensities of both lines increase. In contrast to that in mixture (II) the intensities decrease with increasing temperature.

The main content of the samples is most surely the 123-phase. Also the existence of the "green phase" (211) is clearly visible. Surprisingly also other phases are detectable: The DTA-curves suggest the existence of 011 and 001, whereas the XRD-curve only reveals peaks corresponding to the 011-phase.

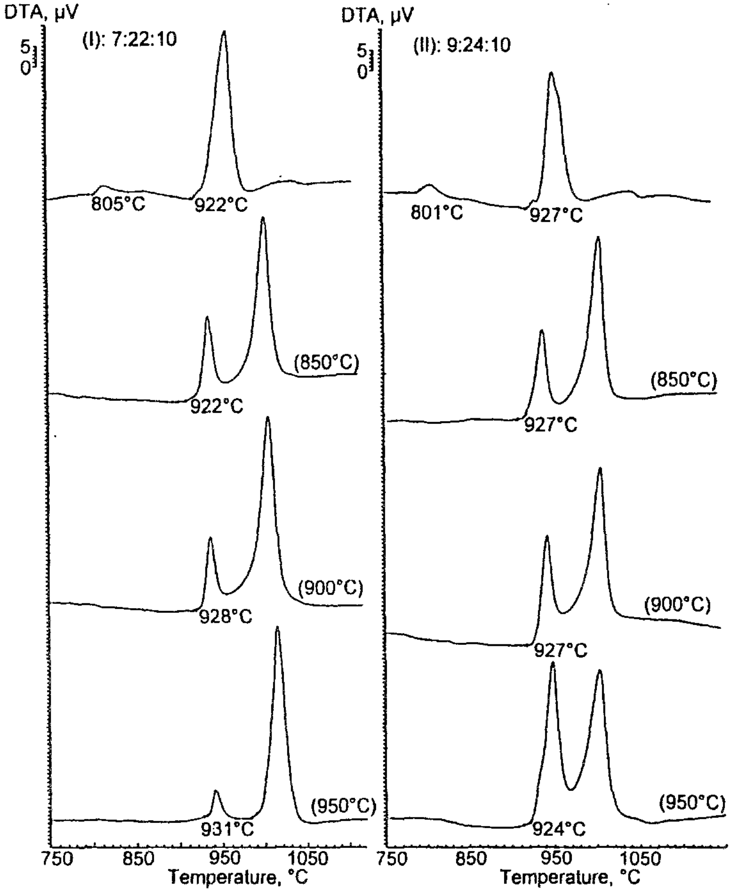

Fig. 10 DTA-curves of untreated (a, e) and pre-treated reactive mixtures, i.e. 850°C (b, f), 900°C (c, g) and 950°C (d, h)

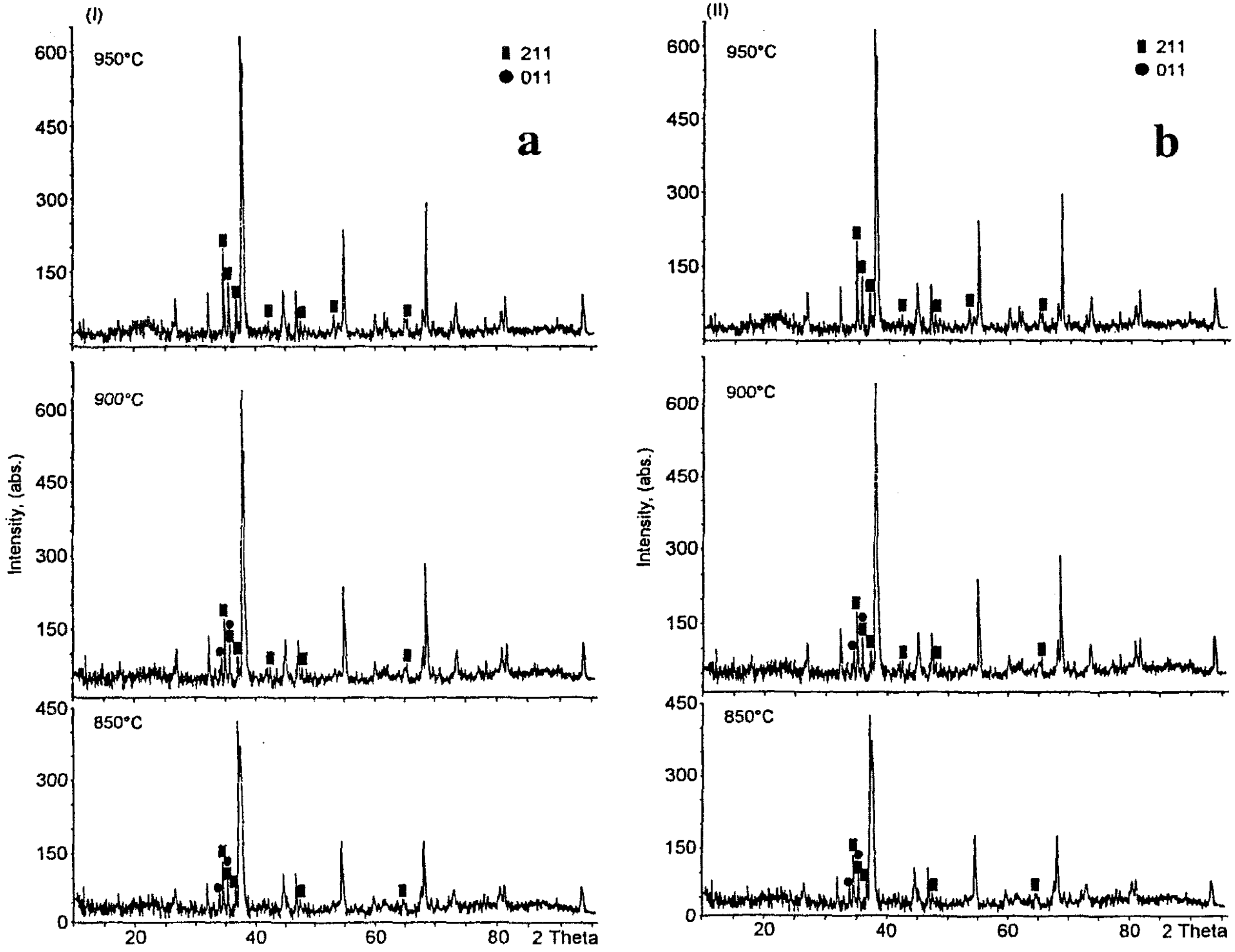

Fig. 11 X-ray-diffraction diagrams of the previously treated mixtures (I) and (II)

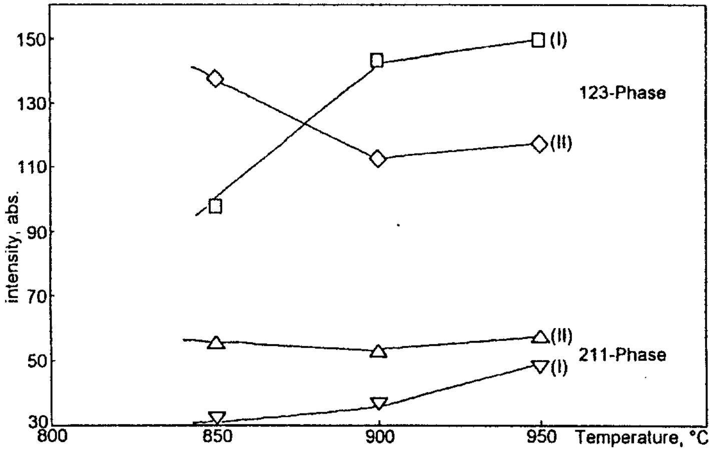

Fig. 12 Comparison of the intensities of the strongest X-ray lines of $YBa_2Cu_3O_{7-x}$ (No.103) and Y_2BaCuO_5 (No.131)

Conclusions

In the regarded reactive 123-precursors solid state reactions start at about 600°C. On further increase of the temperature at first $Y_2Cu_2O_5$ is formed then Y_2BaCuO_5 and finally $YBa_2Cu_3O_{7-x}$ – it confirms the experimental results of Ruckenstein *et al.* [8] and Wu and Chang [22]. At temperatures exceeding 915°C a partial liquid phase occurs, mainly consisting of $BaCuO_2$ and CuO.

Pure-phased 123 shows a special thermal behaviour, characterized by the endothermal effect at 1020°C (peritectic melting) in the first place. The existence of secondary phases shifts this peak towards lower temperatures and causes additional effects at temperatures ranging from 910–950°C, what has already been observed [20]. Reactive mixtures seem to behave similar to impure 123-phase: 123-phase is formed upon heating and the non-reacted residual phases show melting effects – in combination with the 123-phase or seperately. The influencing parameters are: purity, composition and grain-size of the precursor.

Carbon, occurring as an unwelcome impurity in the 011 or 123-phase, changes the reactivity of the mixtures and increases the porosity of melt-processed samples.

By changing the stoichiometrical composition of the precursor mixture, melt-processing can be improved. A resulting dispersion of 211 or 001 phase in the 123-matrix is even desired, since it can improve the properties of the superconductor.

Concerning the variation of the grain sizes of the precursors it is to say, that it has an effect on the reactivity of the samples but not on the peak onset temperatures.

In melt-processes the heating rate has an influence on the phases formed during heating. An increase reduces the amount of 123-phase formed during the heating step. Size and dispersion of 211-inclusions can thus be determined indirectly, by utilizing the different behaviour of peritectically and solid state-grown 211-particles. With no 123-phase having formed via solid state reaction there are no peritectically grown 211-crystals in the sample after processing. Adding a stoichiometrical surplus of yttria to the precursor could possibly lead to a size of the 211-inclusions that is determined by the size of the precursor powder.

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