JOURNAL OF MATERIALS SCIENCE 30 (1995) 2055–2060

Reactivity and powder morphology in $YBa_2Cu_4O_8$-related compounds synthesis

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The factors that allow the synthesis of $YBa_2Cu_4O_8$ at low oxygen pressures are discussed. The importance of having a homogeneous distribution of initial reacting powders to increase the reaction speed and purity of the final product is shown. Compounds with partial and total substitution of yttrium by thulium are also considered.

1. Introduction

$YBa_2Cu_4O_8$ (124) is a member of a family of superconducting compounds, with the general formula $Y_2Ba_4Cu_{6+n}O_{14+n}$ ($n = 0, 2$); it has a lower critical transition temperature, T_c, than the $n = 0$ member of the family, but it has the advantage of having stable oxygen stoichiometry, and does not form twins due to structural phase transitions during cooling down after high temperature synthesis, thus making this a technologically interesting material.

124 can be synthesized through several different routes. The first bulk synthesis was performed at oxygen pressures exceeding 405 MPa [1]. It was soon discovered that these materials also could be produced at low oxygen pressure. One atmosphere oxygen pressure synthesis is possible because at low enough temperatures, i.e. less than 860 °C, 124 is the stable compound for the corresponding stoichiometric composition of oxides [2]. Nevertheless, under the above mentioned conditions, and starting either with $YBa_2Cu_3O_{7-x}$ (123) and CuO or from simple stoichiometric mixtures of the oxides, the reaction is very slow and CuO traces can always be detected in the final products, even though very finely divided reagents are present in the initial mixture [3, 4]. The reaction speed can be increased and the maximum temperature of heat treatment can be lowered by the addition of alkali carbonates. In this case, however, alumina high temperature reaction chambers and crucibles must be avoided because they react with the alkali carbonates, and product contamination with aluminum is difficult to avoid. This method gives less CuO impurities in the final product [5]. Other methods which start from nitrates [3, 6] or use special procedures to mix and mill the initial reagents [7] give a purer product. High purity 124 can be produced after only 92 h heat treatment at 1 MPa oxygen pressure, starting from oxides and carbonates treated with HNO_3 to get the corresponding nitrates, provided that intermediate milling of the reacting powders is performed during the heating-up procedure [8].

The general strategy followed to favour the formation of the desired phase and to increase the reaction efficiency is to develop a method which achieves a homogeneous mixture of the initial reagents, followed by high temperature solid state reaction. The grain size of the reaction powders and its distribution are shown to play major roles in the success of the reaction. In this paper, more than one procedure for the synthesis of $YBa_2Cu_4O_8$ at low oxygen pressure is taken into account to establish the validity of the general strategy outlined above for the present family of compounds. For comparison the synthesis of compounds containing thulium in partial or total substitution for yttrium is also considered; in particular, $Y_{1-x}Tm_xBa_2Cu_4O_8$ with $x = 0.1$, 0.3 and 1.

2. Experimental procedure

Three samples with 124 nominal formula were prepared following the procedures described in [4, 8]. Briefly:

1. Stoichiometric quantities of CuO, $BaCO_3$ and Y_2O_3 are mixed in a beaker with concentrated HNO_3; the corresponding nitrates are formed. This liquid phase is then slowly heated in several steps up to 170 °C and is brought to dryness. The powders are mixed manually in an agate mortar. The sample is then heat treated for 2 h at 600 °C, for 2 h at 800 °C, twice for 20 h at 820 °C, and finally for 40 h at 820 °C. Every heat treatment is performed in flowing oxygen at 1 MPa pressure. Between each treatment the powders are milled. This will be called sample A.
2. Equal moles of 123 and $Cu(NO_3)_2 \cdot 3H_2O$ are mixed and milled. Several heat treatments in oxygen atmosphere are performed, following the timing and temperatures of procedure 1. This will be called sample B.
3. Stoichiometric quantities of 123 and CuO powders with typical grain sizes below 0.5 μm, obtained by oxidation of copper nitrate, are carefully mixed and milled. The atmosphere and heat treatment are the same as in procedure 1. This will be called sample C.

The samples with thulium are prepared following procedure 1, just by changing yttrium oxide with Tm_2O_3. The sample with nominal formula

$TmBa_2Cu_4O_8$(Tm–124), prepared following procedure 1, will be denoted sample D.

All treatments are performed in alumina crucibles. In all procedures, after each heat treatment above 600 °C, the powders are carefully mixed and milled in an agate ball mill for 2 h. Thulium nitrate hydrate is prepared by reacting Tm_2O_3 with an excess of concentrated HNO_3 and then drying the resulting solution. Characterization of the reaction products is made at each step of the thermal cycle. The powder morphology and the degree of mixing are recorded with a scanning electron microscope (SEM) and their chemical composition with the analysis of their energy dispersion spectra (EDX). The EDX are calibrated using X-ray pure 123 to define the yttrium, barium and copper peak concentration dependence to give more reliable quantitative results. For this analysis the powders are pressed in pellets at 7091 MPa using cylinders with surfaces polished to optical quality; no surface decoration with a conducting material was needed. From the secondary electron images of the surface of the pellets it is evident that voids are present which may limit the precision of the EDX microanalysis. These measurements are performed with a Jeol 820 scanning electron microscope.

The phases resulting from the reactions at the different steps of each procedure are identified by XRD analysis, which is performed with a Philips PW 1830 powder diffractometer. The thermal analysis is made with a Netzsch 409 thermal system.

3. Results

A first comparison among the different samples is made after 4 h heat treatment: SEM images show that there is a strong difference in morphology: see Fig. 1a–d, corresponding to samples A, B, C and D, respectively. For samples A and D, both made following procedure 1, the grain sizes vary in the range between 0.1 to 1 µm, while for samples B and C submicron grains are mixed with grains of a few micrometers. For samples B and C the EDX analysis shows that the larger grains correspond to the 123 composition. In sample C small grains correspond to CuO, while in sample B all the elements involved in the 124 chemical formula are present. According to what is known from [8], in these grains there should be oxides of the corresponding elements coming from the oxidation of $BaNO_3$, $Y(NO_3)_3 \cdot zH_2O$ and $Cu_2(OH)_3NO_3$. These last compounds result from reaction between 123 and $Cu(NO_3)_2 \cdot zH_2O$ [8]. In these two samples some grains show a lamellar morphology, particularly in sample B. This is not surprising because the 123 reagent has a lamellar structure.

After heat treatment at 800 °C, X-ray spectra clearly show, for samples B and C, that only CuO and 123 are present in the powders. Analysis of the XRD spectra for samples A and D indicates that the nitrates of the corresponding elements were converted, as expected, to oxides.

At this stage of the reaction the degree of mixing of the reagents can be analysed by the backscattered electron image. Consider the images of sample C:

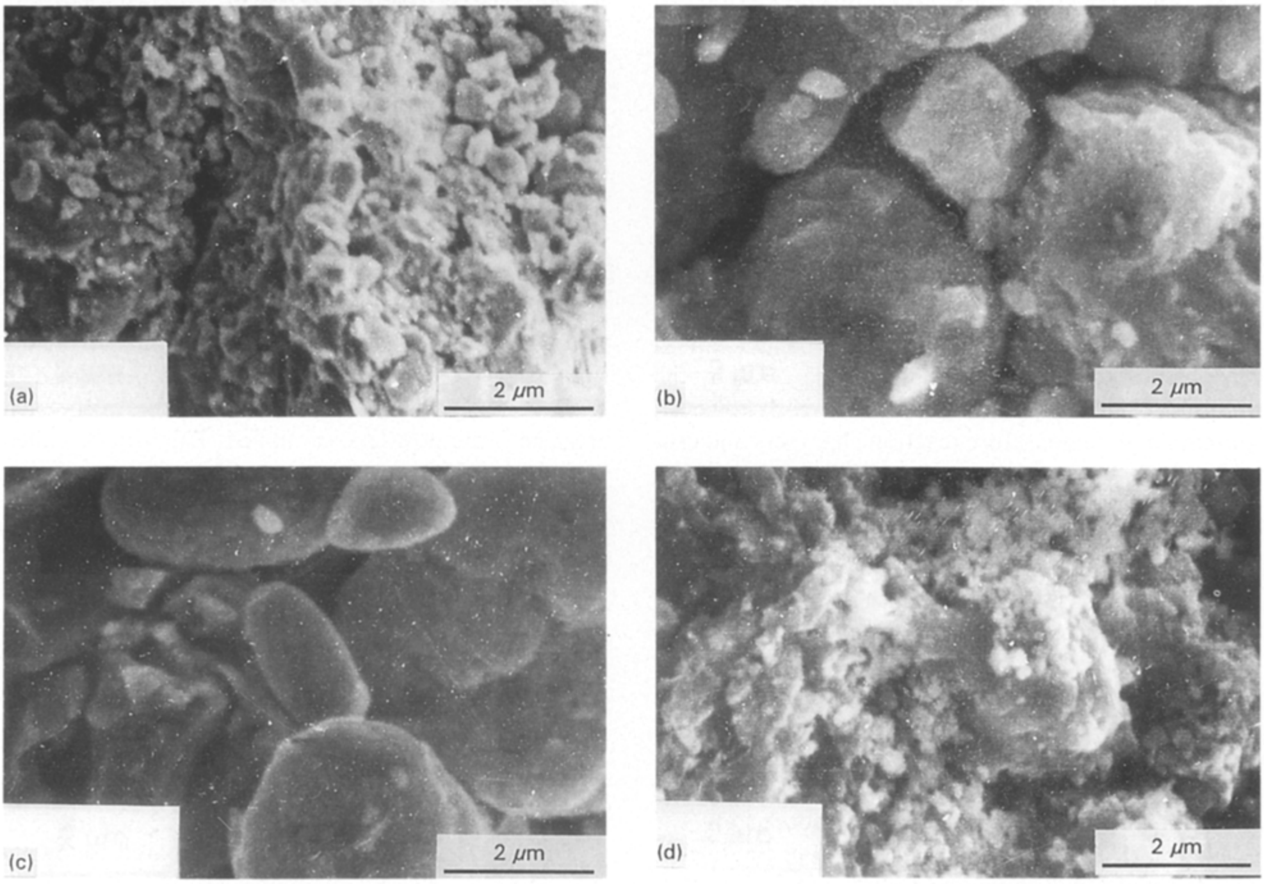

Figure 1 SEM images of samples A, B, C and D after 4 h treatment.

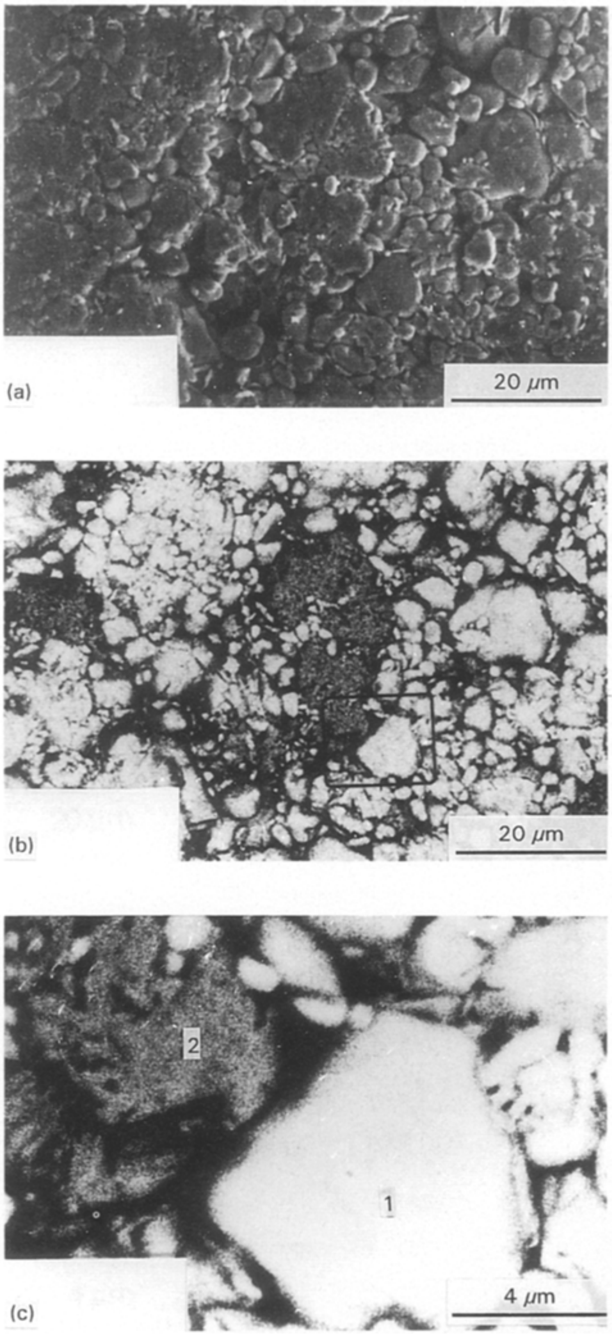

Figure 2 (a) SEM image of sample C; (b) BE image corresponding to the same zone as Fig. 2a; (c) enhancement of the region of Fig. 2b where the EDX analysis was performed.

Fig. 2a is an SEM image of the sample whereas Fig. 2b is a backscattered electron (BE) image where light and dark regions can be easily identified. From EDX analysis it appears that the light (dark) spots are associated to the presence (absence) of Ba and Y. The dark regions contain only Cu and O, while the elemental composition of the light one is Y : Ba : Cu $\approx$ 1.1 : 2 : 3, i.e. the elemental composition of 123 measured within the precision of the technique. Fig. 2c shows the regions where the EDX analysis was performed.

The presence of oxygen is detected throughout the sample, but the quantitative analysis is not reliable. Since the dimensions of the 123 and CuO regions vary from 1 μm up to 10–20 μm, the homogeneity of the two reagents is only at the micrometre level (even if the grains, at least for CuO, have sizes below 0.5 μm). This slows down the reaction considerably, because diffusion of CuO in the 123 regions has to take place over one or more micrometres.

Consider now the morphology of sample B after 800 °C heat treatment: even if there are some large grains in the 10 μm scale, most of the material is finely divided, as shown in Fig. 3; this BE image indicates that the distribution of its chemical elements is more uniform than in sample C. It is not possible to analyse rigorously by EDX all the regions of different darkness that can be distinguished, because the dimensions of the light spots expected to correspond to the yttrium or barium-containing regions are under the resolution limit of this technique (~ 1 μm). However, it is important to observe that wherever quantitative analysis is feasible, even if it does not give the same numerical result, it shows the presence of all the chemical elements in all the different spots.

Sample A, after 800 °C heat treatment, has grain sizes below 1 μm, and all the chemical elements are present on the 1 μm scale; no region of different contrast can be identified on BE images or can significant differences in the EDX analysis be observed. An analogous description can be made for sample D.

It is useful to sum-up the results up to this stage of evolution of the reaction for the different procedures: it is established that both EDX and BE analyses show that the chemical elements in sample C are not homogeneously distributed. In the case of sample B, backscattered electron images show that the elements are not evenly distributed, even if at the micrometre length scale all the elements are present in all regions, as shown by EDX analysis. Finally, both EDX and BE images show that samples A and D are the ones where the elements are better distributed.

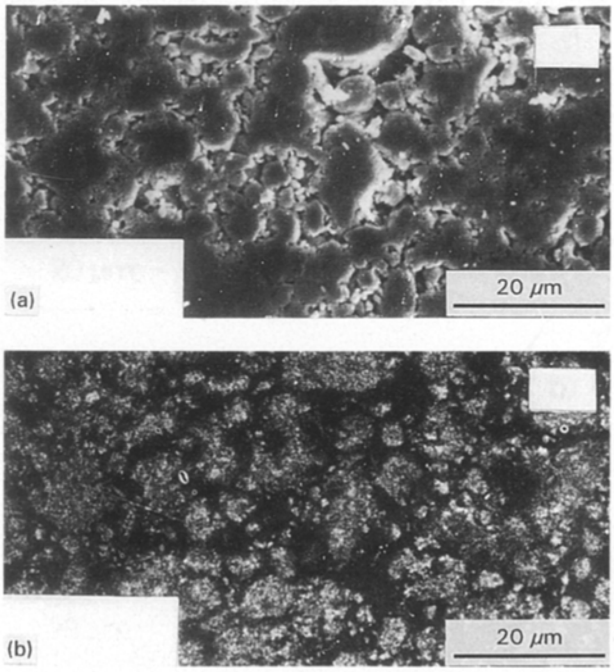

Figure 3 (a) SEM image of sample B after 800 °C heat treatment. The BE image, (b), shows that the elements are not homogeneously distributed.

The analysis after 84 h heat treatment gives no major changes for sample C; the large grains present after 4 h treatment (Fig. 1c) break down, but EDX and BE analyses indicate that there is no significant chemical mixing, and the XRD spectrum confirms that the reaction has just begun (since CuO and 123 are still the major phases while 124 is only a minor one, as can be seen in Fig. 4).

Sample B, at the same step of the heat treatment, shows a strong reduction of grain dimension along with the formation of a lamellar morphology. At this stage XRD clearly indicates that 124 is the majority phase, but there are peaks still present corresponding to CuO, Y_2BaCuO_5 and also 123 (see the XRD spectrum corresponding to sample B in Fig. 4). This last identification is difficult because of spectral interference from other substances. The situation is totally different in the case of sample A: after two treatments of 20 h at 820 °C, sample A starts showing the X-ray spectra of 124 [8] and after 84 h treatment, SEM images clearly show the formation of very small crystallites (Fig. 5). Comparison between X-ray spectra of samples A, B and C after 84 h heat treatment shows that in sample A the reaction is highly enhanced, see the corresponding spectrum in Fig. 4.

Consider now the thulium containing samples. Following procedure 1 it was possible to synthesize $Y_{(1-x)}Tm_xBa_2Cu_4O_8$ with $x = 0.1$ and 0.3. The compound with $x = 0.1$ has similar behaviour to sample A, whereas the time needed to obtain a pure phase of the $x = 0.3$ compound is around 300 h. The synthesis of pure $TmBa_2Cu_4O_8$ following procedure 1 was attempted without success. Even after 800 h treatment the X-ray diffractogram indicated the presence of large amounts of Tm_2BaCuO_5 together with $TmBa_2Cu_4O_8$ and other impurities which were not identified. In this case the presence of so many phases was surprising because, as was described earlier, the reacting powders, after 4 h of treatment, were as small and as well distributed as those in sample A, compare Fig. 1a and d. Moreover, EDX analysis after 84 h heat treatment indicates that the chemical elements are distributed over the whole sample, and only homogeneous zones are seen with BE for both samples A and D. Nevertheless, XRD demonstrates that sample D is a mixture of different compounds, whereas sample A is pure 124.

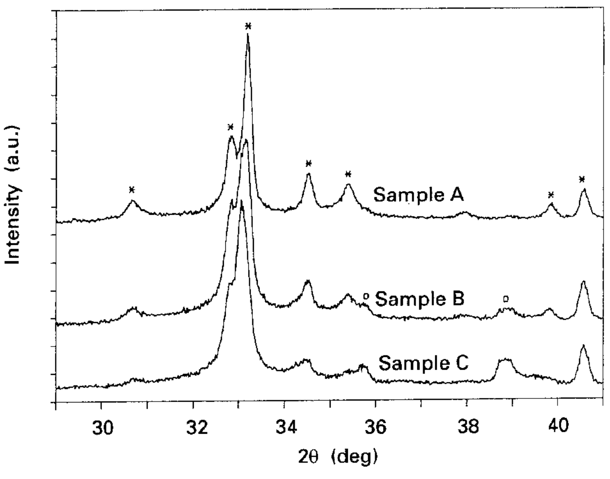

Figure 4 XRD spectra of samples A, B, C and D, respectively, after 84 h heat treatment: (*) $YBa_2Cu_4O_8$, (O) CuO.

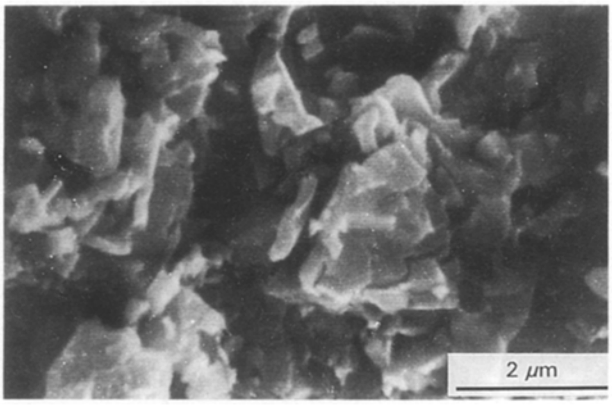

Figure 5 SEM image of sample A after 84 h treatment.

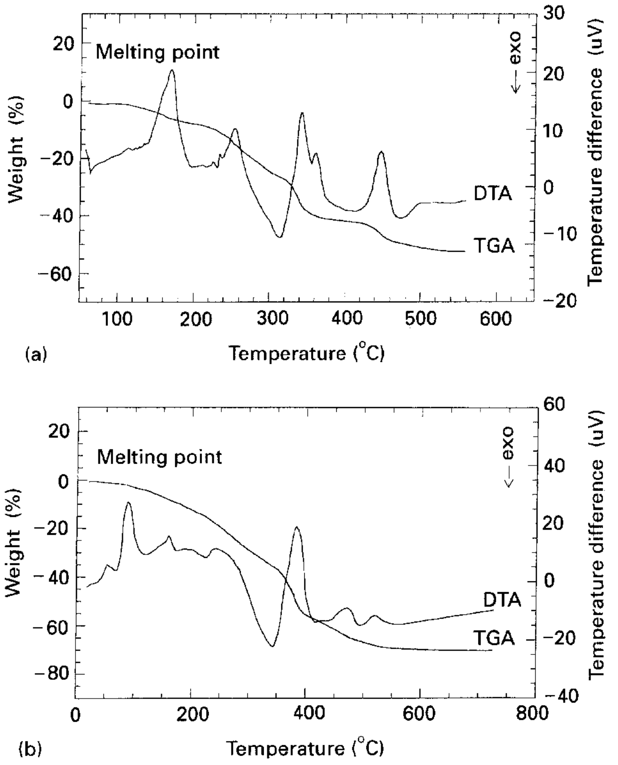

Figure 6 TGA and DTA analysis of (a) $Tm(NO_3)\cdot 2.5\ H_2O$, and $Y(NO_3)\cdot 5H_2O$.

At this point it was necessary to understand the reasons for the different qualitative results. A first step was to study the behaviour of the reagents during the heating-up process. It indicated t hat the main difference, following procedure 1, for the two samples under consideration has to do with the state of aggregation of the various reagents in the temperature interval 80–220 °C. In particular, thulium nitrate is in the liquid state only above 167 °C, whereas yttrium nitrate is already liquid at 88 °C. In Fig. 6a are given the thermogravimetric (TGA) and differential thermal analyses (DTA) of $Tm(NO_3)_3\cdot zH_2O$ and in Fig. 6b the same plots are shown for $Y(NO_3)_3\cdot 5H_2O$. An easy calculation gives $z = 2.5$.

The different melting points of the two nitrates are relevant to the homogeneity of the resulting powders coming from the conversion of the nitrates to oxides. In the case of sample A there is a temperature interval between 114 and 170 °C, where both yttrium and copper nitrates are in the liquid state and mix together; whereas for sample D there is no temperature interval where there are two nitrates in the liquid state: at 167 °C copper nitrate is almost completely converted to $Cu_2(OH)_3NO_3$, a powder, so in this last case the mixture between the reagents is, at best, between a liquid and two powders. Above 170 °C, decomposition and oxidation processes of the reagents follow similar paths for both samples, and no major differences can be reported.

4. Discussion

From the preceding results the importance of the reciprocal dispersion of reagents in the synthesis of $YBa_2Cu_4O_8$ at low oxygen pressure is clear. EDX analysis and BE images indicate that at early stages the most uniform distribution of the chemical substances is reached through procedure 1, which is the fastest procedure, as well as the one that gives the purest 124 [8]. Procedure 3, which does not achieve a homogeneous distribution of the initial reagents, gives the largest quantity of impurity phase for a fixed reaction time and has the slowest reaction speed to achieve the 124 product, even though the initial powders have submicrometre CuO grains.

These results clarify that it is not enough to have small grains of the initial reagents, but it is also important that they are homogeneously dispersed, i.e. the diffusion processes dominate the reaction speed at the temperatures under consideration. This is not surprising; in fact it is known that solid state reactions can be dominated by diffusion processes [9, 10]. However, there are also other factors that may be important, particularly the similarity of the structure of the initial reagents with that of the products. The present work shows that this is not the case, otherwise procedure 3 would have given a faster reaction speed than procedures 1 and 2 because of similarities in the structure between 123 and 124.

The degree of homogeneity of the reagents in the first three steps of the procedure appears to be crucial. In fact, EDX and BE analyses after only 4 h allow the establishment of a correlation between reaction efficiency and the degree of homogeneity of the reagent mixture for each procedure. It can be concluded that a way to improve the reaction times of all procedures is to mill with a liquid medium to improve the mixing of the initial powders. In the case of $TmBa_2Cu_4O_8$, however, the distribution of the initial powders and their size are not the only crucial factors for phase formation: both EDX and BE analyses show for yttrium and thulium containing initial reagents, a similar and homogeneous chemical distribution and mixing of reagents and intermediates. Therefore the different yields of the reaction in the two cases show that the conclusion of the diffusion-limited process cannot be extended to all the rare earth substituted 124-like compounds, unless the hypothesis is made that diffusion processes are relevant for length scales below the resolution of the BE images. It may happen that procedure 1 has to be modified to synthesize $TmBa_2Cu_4O_8$, because the thermal analyses of thulium and yttrium nitrates (Fig. 6a, b) indicate in the synthesis of Tm–124 the favourable condition of having two reagents present simultaneously in the liquid phase does not occur, as happens with the 124 synthesis.

The reason for the negative results of the synthesis of pure Tm–124 could also be attributed to the particular stability of Tm_2BaCuO_5 which is favoured by thulium rich zones, which can be present if, during synthesis, the rare earth nitrate segregates. If this is the case, segregation must happen at a length scale below 1 μm because it is not shown by EDX analysis.

Finally, some considerations on phase stability. It is known that 124-like systems made by totally substituting dysprosium and holmium to yttrium have a pressure–temperature stability range similar to 124, but for europium and gadolinium substitution the stability range shifts to higher pressures [11]. As far as is known there are no reports on the stability range of thulium containing materials. In this work it is demonstrated that compounds of the general formula $Y_{(1-x)}Tm_xBa_2Cu_4O_8$, with $x \leqslant 0.3$, are stable at 1 MPa oxygen pressure and 820 °C. Moreover, Tm–124 can be obtained at the preceding pressure and temperature, following procedure 1, but not in pure form.

In conclusion, it is shown that homogeneous dispersion of all the reagents in the low temperature, low oxygen pressure synthesis of 124 is the most important aspect to be taken into consideration. It is also shown that the synthesis of thulium doped 124 compounds is possible, at least for atomic substitution of thulium for yttrium up to 30%. The synthesis of pure Tm–124 was not achieved. A possible reason for this failure is the formation of Tm_2BaCuO_5, which does not react to give Tm–124 as easily as in yttrium containing compounds. Slower reaction kinetics cannot be ruled out though, because the reaction time grows for increasing thulium doping.

Acknowledgements

The authors thank Mr Sandro Bertoni from Enichem–Istituto Guido Donegani for useful discussions and SEM measurements.

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Received 9 February
and accepted 24 August 1994